

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry
IN ALL ITS APPLICATIONS TO
PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

WILLIAM CROOKES, F.R.S., &c.



VOLUME LIV.—1886.



LONDON:
PUBLISHED AT THE OFFICE, BOY COURT, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCLXXXVII.

THE CHEMICAL NEWS.

VOLUME LIV.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1388.—JULY 2, 1886.

NOTE ON A METHOD OF ILLUSTRATING THE PERIODIC LAW.

By J. EMERSON REYNOLDS, M.D., F.R.S.
Professor of Chemistry, University of Dublin.

THE annexed woodcut is a reproduction of a diagram which has been used in my lecture-room for some years in order to illustrate the periodic character of the relation between the atomic weights and properties of the chemical elements. It was not intended for publication, but some scientific friends considered it likely to prove useful and suggestive outside the limits of a University theatre: hence this note.

The curve represented is intended to give a special picture of the general relations of the elements, and its foundation is Mendeleeff's well-known tabular classification in which he applies and greatly extends the important periodic principle recognised by Newland.

Every chemist is familiar with the annexed table, but it is given to save the trouble of reference elsewhere.

The details of this classification are so well known through the numerous and important papers of Dr. Carnelley and others that it is unnecessary to discuss them here. It will suffice to point out that the chief features are—

- 1st. The arrangement of the elements according to atomic weight in twelve "series," or "periods" of seven (or in some cases ten) members each. These are found on the same horizontal line.
- 2nd. The division of the elements which occupy similar positions in the respective periods into "groups" of analogous bodies. These are found in the same vertical column, and there are eight such groups, as the exceptional members of Mendeleeff's "long" or ten-member periods form the eighth group.
- 3rd. The distinction of the periods into two classes, "odd" and "even," since the corresponding members of *alternate* periods are found to resemble each other more closely than those they immediately succeed or precede.

When we carefully consider the relations of the members of the "periods" it is found that the general properties of the elements vary from one to another with tolerable regularity until the seventh member is reached, which latter is in more or less direct *contrast* with the first element of the same period, and with that of the next. Thus chlorine—which is the seventh member of Mendeleeff's third period—is in chemical contrast with sodium, the first member of the same series, and also with potassium, which is the first member of the next series. On

the other hand, sodium and potassium are analogous forms of matter. Now the six elements whose atomic weights lie between those of sodium and potassium vary in properties from one member to another until the sodium contrast—chlorine—is reached; but from chlorine to the sodium analogue—potassium—the change in properties appears to take place *per saltum*. Similar alternations of gradual and abrupt changes in properties are observed as the atomic weights increase.

The real distinction just pointed out seems to have attracted singularly little attention in the construction of the curves or spirals which are intended to illustrate the relations of the elements in accordance with the periodic principle, yet its recognition is essential if we are to form an adequate mental picture of the relations in question: the particular direction it gives to our conceptions will presently appear.

If the relations of the elements within each period are now considered with a view to graphic translation, it is evident that the recognition of more or less contrast in properties between the first and last members of each series implies the existence of a position of mean variation or transition within each system.

On further comparing the members of the periods, it is found that the *fourth* element of each series in general possesses the properties which a transition member might be expected to exhibit. Thus silicon may be represented at the apex of a tolerably symmetrical curve which should represent for the particular period the direction in which the properties of the series of elements vary with rising atomic weight.

A physical analogy will help to make the meaning of this clear:—

Let the line A B (Fig. 1.) represent part of a string in tension, and *a, b, c, d, e, f,* and *g* seven knots upon it. The string is now thrown into a number of vibrating segments: *o* and *o'* represent two nodal points, between which one segmental vibration takes place. The several knots oscillate rapidly to and fro in the direction of the dotted lines, *a* moving from the position of rest to *a'* and back again, when it swings to the same extent on the opposite side of the line A B, returns, and starts afresh. Each knot performs similar journeys, but the lengths of the paths vary: thus the length increases from *a* to *b*, from *b* to *c*, and from *c* to *d*, while it diminishes from *d* to *e*, *e* to *f*, and *f* to *g*. The knot *d* is therefore exceptional, in that it suffers the maximum displacement from the mean position; the knots *c* and *e* perform journeys of comparable lengths, but they are otherwise in more or less direct contrast; similarly *b* and *f*, *e* and *g*, form contrasted pairs.

Let the knots in the string represent the atomic groupings we call elements, arranged in the order of

Series or Period.	Group I. R ₂ O	Group II. RO	Group III. R ₂ O ₃	Group IV. RH ₄ RO ₂	Group V. RH ₅ R ₂ O ₅	Group VI. RH ₆ RO ₃	Group VII. RH R ₂ O ₇	Group VIII. RO ₄
1	H = 1							
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Ni = 58.5, Co = 59
5	Cu = 63	Zn = 65	Ga = 69	— = 72	As = 75	Se = 79	Br = 80	
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96	— = 100	Rh = 104, Ru = 104.5
7	Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 121	Te = 125	I = 127	Pd = 106
8	Cs = 133	Ba = 137	La = 139	Ce = 141	Di = 144	—	—	—
9	(—)				Er = 166	—	—	—
10					Ta = 182	W = 184	—	Ir = 192.5, Os = 193
11	Au = 196	H ₃ = 200	Tl = 204	Pb = 207	Bi = 208	—	—	Pt = 194.5
12				Th = 233	—	U = 240	—	—

atomic weight* rising from *a* to *g*, and we have a picture of a "period" of seven elements regarded as a vibrating system. Unlike most analogies, this one bears tolerably close examination.

Thus, if we take any well-defined periods, such as the two following,—

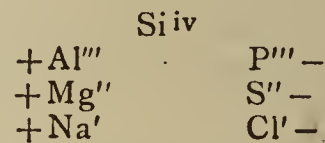
2.—Li = 7, Be = 9, B = 11, C = 12, N = 14, O = 16, F = 19
3.—Na = 23, Mg = 24, Al = 27, Si = 28, P = 31, S = 32, Cl = 35.5

we find that the *fourth* member naturally divides the particular period in two parts. In the period 2 carbon is the middle term, and in 3 silicon. Corresponding elements to these can be found in nearly all the succeeding periods,

* Of course this arrangement is not necessarily symmetrical, as supposed in the case of the knotted string.

and their properties in relation to those of the members of the same period which immediately precede and follow them are on the whole exceptional. They afford strongly marked dioxides whose hydrates exhibit very feeble acid properties, and in all the best known periods they appear as transition elements between two sub-groups of three each. I propose to distinguish such bodies as *meso-elements* to avoid needless repetition. Now the meso-element of a period is analogous to the knot *d* when at its maximum displacement.

If we examine a particular period—for instance, that one whose meso-element is silicon—we note:—*First*, that the three elements of lower atomic weight than silicon, viz., sodium, magnesium, and aluminium, are distinctly *electro-positive* in character, while those of higher atomic weight, viz., phosphorus, sulphur, and chlorine, are as distinctly *electro-negative*. Throughout the best-known periods this remarkable subdivision is observable, although, as might be anticipated, the differences become less strongly marked as the atomic weights increase. *Secondly*, that the members above and below the meso-element fall into pairs of elements, which, while exhibiting certain analogies, are generally in more or less direct chemical contrast. Thus, in the silicon period we have—



This division also happens, in many cases, to coincide with some characteristic valence* of the contrasted elements. It is noteworthy, however, that the members on the electro-negative side exhibit the most marked tendency to variation in atom-fixing power, so that valence alone is an untrustworthy guide to the probable position of an element in a period.

The pairs of more or less contrasted elements may be likened to the pairs of knots on the string whose paths of vibration are of approximately equal length; but it is convenient for the purpose of graphic illustration to assume that the paths of each pair are of the same length, or that the displacements are in the ratio of 1:2:3:4,—that of *d'*, Fig. 1, which is the longest. On reference to the diagram, Fig. 2, the nature of this arrangement will be evident, and the portions when connected as shown are seen to form an expanding curve such as would be afforded by a string or chain† whose parts are in unequal tension. With the aid of the scale A B there is no difficulty in picturing the elements in the positions of the knots on the string, and so regarding them as members of a vibrating system. All the elements whose constants are well known find places on the curve.‡

Thus the physical analogy helps us to form some conception of the relations of the members of the periods, and of the latter to one another. Moreover, the admission of the periodic principle at all seems to require the recognition of similar relations to those indicated.

It will now be interesting to note some of the points suggested by the foregoing considerations:—

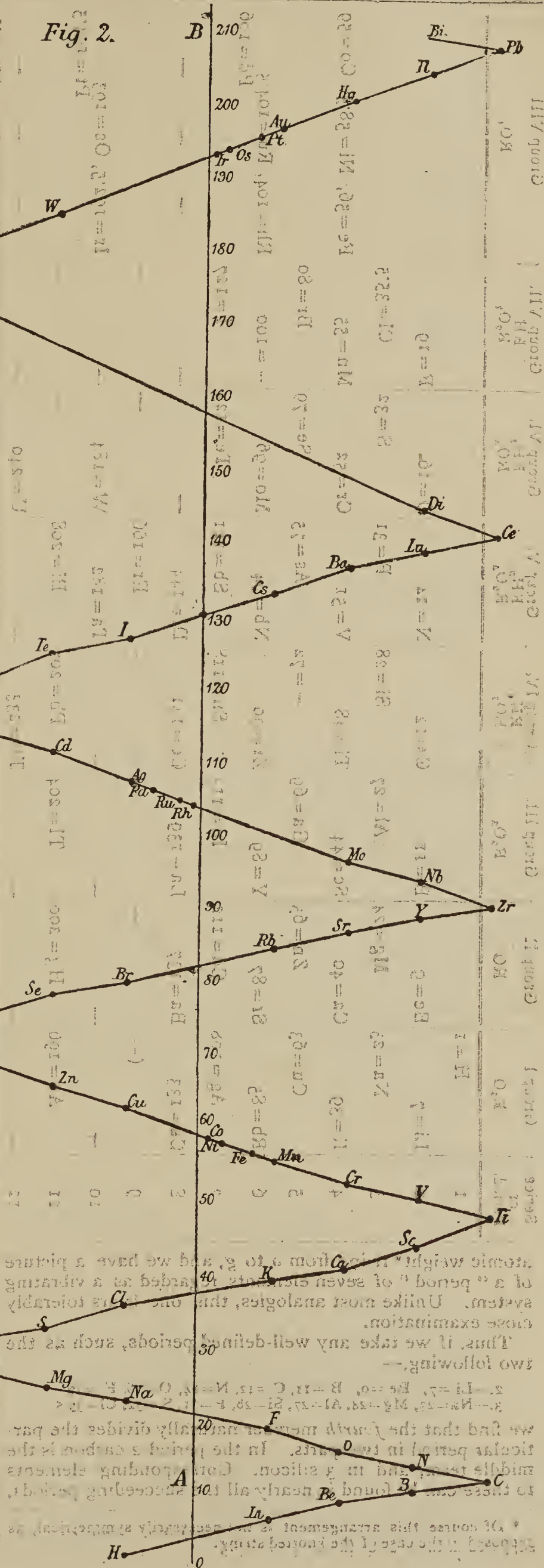
1. If we picture the elements as members of some such vibrating system as supposed, difficulties of the kind noted in the case of the relations of chlorine to potassium disappear, since the potassium knot is in a complementary position to that of chlorine, and is in a certain sense in direct contrast.
2. On Mendeleeff's system hydrogen is the solitary representative of his first period, and it seems to have

* This term is here used in the wide sense in which it was employed by Wurtz.

† My friend Prof. Fitzgerald, F.R.S., suggests that a vibrating metallic chain, suspended from the ceiling and attached to the floor, would afford a more complete picture, as the regular and considerable changes of tension, due to the increasing weight, would lead to the production of regularly expanding loops.

‡ The length of the page of the CHEMICAL NEWS prevents the representation of thorium (233) and uranium (240), but they fall naturally into position on an extension of the curve.

Fig. 2.



been assumed that the other six members (hypothetical) must have atomic weights between 1 and 7. If, however, we allow the form of the curve to influence our judgment, the position of hydrogen in reference to lithium is rather that of the *last* member of one period to the first of another. Hence, if hydrogen is really a member of a period of seven elements, and the seventh member, the remaining six must have atomic weights less than that of hydrogen. There is therefore room for Lockyer's "helium," and for the element that Dumas' modification of Prout's law demands.

3. The "odd" and "even" periods of Mendeleeff are at once distinguished: thus, while the knots representing the carbon period are at the extreme limit on one side of the mean position A B, those of the silicon period are necessarily at corresponding points on the *opposite* side. The strictly analogous periods are therefore found on the *same* side of the line A B, and elements found at *similar points* on the curve should form a homologous series. For example: Mg, Zn, and Cd are members of such a series on one side, while Ca, Sr, and Ba form a similar group on the other; the two groups of homologues exhibiting, at the same time, the many cross relations we should expect.
4. The general contour of the curve is such that we are not permitted to assume the existence of Mendeleeff's *ninth* period (see table *supra*). This is remarkable, as six out of these seven elements postulated by Mendeleeff are admittedly unknown, while the single known element supposed to belong to the period is erbium. Now, even if the atomic weight of erbium be 166, as supposed, it is obviously possible to find a place for the element in the period which includes tantalum and tungsten, so that it is not necessary to assume the existence of a whole period in order to find a place for erbium. But it is doubtful whether the constants of the *pure* element are yet sufficiently known to justify a decision between the two points that can be selected for it.
5. As the eye traces the curve from hydrogen upwards it is seen that near to *three* out of the ten nodal points the symbols of the elements which form Mendeleeff's "eighth group" are to be found. These bodies are obviously *interperiodic*, in the sense that their atomic weights necessarily exclude them from the periods into which the other elements fall, while their chemical relations with certain members of the adjacent periods lead to the conclusion that they are interperiodic in the special sense of being transitional as well.

This "group," so-called, is divisible into three triplets, which are as follow:—

First.	Second.	Third.
Iron = 56.	Rhodium = 104.	Iridium = 192.5.
Nickel = 58.5	Ruthenium = 104.5.	Osmium = 193.
Cobalt = 59.	Palladium = 106.	Platinum = 194.5.

Each triplet seems to form a small period of very closely related elements. It is well known that the members of each triplet so closely approach in atomic weight, present so many physical and chemical characters in common, and are so frequently associated in Nature, that they have often been regarded as probable modifications of a single form of matter. Again, all nine members have low atomic volumes (between 6 and 10), resembling in this respect most of the meso-elements, with which latter, however, they present few other points of similarity. When the scale positions of the triplets are considered they are seen to occur at three points where the known adjacent members of the

periods which form the general system exhibit feeble electro-chemical contrasts—thus, between manganese and copper, the iron triplet appears, between molybdenum and silver the palladium triplet, and between tungsten and gold the platinum triplet. At the corresponding points where the electro-chemical contrasts are very marked—between fluorine and sodium or chlorine and potassium—interperiodic triplets are unknown.

Notwithstanding the exclusion of Mendeleeff's ninth period the diagram shows that a considerable number of elements are still required to complete the system. Doubtless the rare earth metals, when thoroughly identified, will be found to fill some of the vacancies in the periods, just as the new element, germanium, seems to possess most of the properties, predicted by Mendeleeff, of the hypothetical ekasilicon. The discovery of a principle which renders successful prediction possible, as in the cases of gallium, scandium, and germanium, marks a great advance in science, and it is hoped that the mode of picturing the relations of the elements pointed out in this note may facilitate the recognition and application of the principle.

ON THE ATOMIC WEIGHT AND THE SPECTRUM OF GERMANIUM.

By M. LECOQ DE BOISBRAUDRAN.

THE author has just received from Prof. Cl. Winkler, of Freyberg, a fine specimen of germanium. Prof. Winkler was at first inclined to place this body between bismuth and antimony, but he now considers that it should rank between silicon and tin, as the "eka-silicium" in Prof. Mendeleeff's classification. This opinion rests on various important properties of the new metal and on its atomic weight, provisionally fixed at 72.75. M. de Boisbaudran does not undertake to describe this new element which Prof. Winkler is actively studying, but he thinks it may not be uninteresting to give certain observations which confirm M. Winkler's more recent opinion as to the position of germanium in the classification of the elementary bodies.

Long ago, and even before the researches of M. Mendeleeff on this subject, the author had calculated the atomic weight of the hypothetical body intermediate between silicon and tin by means of a classification which has not been published, but which he has often discussed with the regretted J. B. Dumas. He found it 72.28, taking Si = 28 and Sn = 118; M. Mendeleeff gives it as 72 in his table. It is here added in a note that Mr. Newlands had also foreseen the existence of a new element in the series carbon-silicon, and had assigned to it the atomic weight 73.

The author has submitted germanium to the action of the induction spark. There is produced a very fine spectrum which he has not yet had time to examine completely, but which contains two rays of remarkable brightness, a blue and a violet. He has measured these rays with a degree of exactness sufficient for applying his formulæ connecting the wave-lengths of homologous rays and the atomic weights of the bodies which produce them. He has searched for the atomic weight of germanium by this spectroscopic procedure, supposing the element intermediate between silicon and tin.

The homology of the rays is thus established:—

Si.	Gr.	Sn.
1st ray, $\lambda = 412.9$	1st ray, $\lambda = 468.0$	1st ray, $\lambda = 563.0$
2nd „ 389.0	2nd „ 422.6	2nd „ 452.4
Mean 401.0	Mean 445.3	Mean 507.7

If we take as a term of comparison the known series Al—Ga—In we have—

Atomic weights.	Differences.	Variations.
Si 28.0	90.0	
Gr ? between Si and Sn		
Sn 118.0		
Al 27.5		
Ga 69.9	42.4	$\frac{2.8302}{100}$
In 113.5	43.6	

(That is to say 2.8302 per cent must be added to the difference 42.4 to obtain the difference 43.6).

The variation of the increase of the atomic weights is, therefore, 0.028302 in the series Al—Ga—In; the variation of the increase of the wave-lengths is 0.4051 for Si—Gr—Sn and 0.37584 for Al—Ga—In. Following the law which the author has formerly applied to the calculation of the atomic weight of gallium, and which is that in the several natural families the variation of the increase of the atomic weights is proportional to the increase of the wave-lengths of the homologous rays (or groups of rays), taken in what he calls the third harmonic of the spectra. Following this law we have only to put—

Al—Ga—In λ .	Al—Ga—In At. wt.	Si—Gr—Sn λ .	
37.584	: 2.8302	: : 40.51	: x = the variation of the increase of the atomic weights in the series Si—Gr—Sn.

We find $x = 3.051$ per cent.

The increase of the atomic weight from Si to Gr is therefore—

$$\frac{90}{2.03051} = 44.32$$

Whence the series—

Si 28.00	
Gr 72.32	44.32
Sn 118.00	45.68

It will be seen that the number 72.32 agrees well with that, 72.28, which the author had previously deduced from his classification alone. But, on account of the slight uncertainty which exists on the subject of the ray 389 of silicon, we will repeat the same calculation with a single ray for each metal, thus avoiding the use of Si 389, and giving two decimal places to the measurements of λ .

We have then—

Atomic weights.	Wave-lengths. (A single ray, the less refrangible of the two).	Diff.	Variations.
As above, with a single decimal, on account of the uncertainty of the determinations.	Si .. 412.89		
	Gr .. 468.04	55.15	$\frac{72.185}{100}$
	Sn .. 563.00	94.96	
	Al .. 396.10		
	Ga .. 417.05	20.95	$\frac{61.814}{100}$
	In .. 450.95	33.90	

Putting—

Al—Ga—In λ .	Al—Ga—In At. wts.	Si—Gr—Sn λ .	
61.814	: 2.8302	: : 72.185	: x = the variation of the increase of the atomic weights in the series Si—Gr—Sn.

Mean wave-lengths (Two rays).	Differences.	Variations.
Si 401.0		
Gr 445.3	44.3	$\frac{40.51}{100}$
Sn 507.7	62.4	
Al 395.2		
Ga 410.1	14.9	$\frac{37.584}{100}$
In 430.6	20.5	

We find $x = 3.055$ per cent. The increase of the atomic weight from Si to Gr is therefore—

$$\frac{90}{2.033055} = 44.2684, \text{ say } 44.27$$

Whence the series—

Si 28.00	
Gr 72.27	44.27
Sn 118.00	45.73

There is thus a very satisfactory agreement between the provisions of the classification, giving 72.28, and the result of the calculation by the best rays, which is 72.27.

A similar exactness was obtained for gallium previous to any possible determination by the balance.

The classification gave 69.82
Calculation for the rays 69.86
Subsequent gravimetric determination (mean)	69.87

M. Mendeleeff's table assigned the atomic weight 68 to the body situate between Al and In. The difference between the figures of M. Mendeleeff and those of the author is much greater for eka-aluminium than for eka-silicium.

The atomic weights deduced, whether from classification alone or from the calculation of the wave-lengths, depend naturally on the atomic weights or on the wave-lengths and the atomic weights which may be affected by slight errors; it is clear that corrections in the numbers which have served as the bases of these calculations will involve corresponding corrections in the author's theoretic weights. Still these errors ought not to be important, since both for gallium and germanium there is a satisfactory agreement between the data of the author's classification and the results of the application of his special rule.

It will be interesting to see if Professor Winkler will confirm his atomic weight 72.75, or if he will find it approaching 72.3 with a very thoroughly purified specimen.

If germanium has really the atomic weight 72.75, shall we not be warranted in suspecting the accuracy of the atomic weights Si=28.0 and Sn=118.0? — *Comptes Rendus*, vol. cii., No. 23, p. 1291.

NOTES ON THE SOLUBILITY OF THE PHOSPHORIC ACID CONTAINED IN THOMAS SLAG.

By JOSEPH FLETCHER, F.C.S., M.R.I.A.,

Fellow of the Chemical Societies of Berlin and Paris, and
Abstractor to *Chemical Society's Journal*.

YOUR columns have, quite recently, contained a notice of certain experiments on the agricultural value of Thomas slag. The subject has attracted much greater attention in Germany than in this country, and has been experimented on at several of the official agricultural stations.

An excellent *resumé* of what has been done up to the present will be found in *Biedermann's Centralblatt*, vol. xiv., pp. 738 to 756, condensed by Dr. Moritz Fleischer.

The slag when removed from the converters is in pieces of irregular size; exposed to the atmosphere it slowly falls into smaller fragments, emitting the smell of sulphuretted hydrogen. For agricultural purposes it requires to be finely ground,—at least so finely as to pass through a sieve 20 meshes to the inch; it is then a blackish brown powder, containing numerous tabular crystals. Dr. Fleischer thinks that the slag will be found useful as an addition to other manures, but at present he cannot recommend its use alone.

The experiments made with various crops and different mixtures of manures will more properly be the subject of a communication to an agricultural journal; but as its value as a manure will depend on the facility with which the phosphoric acid it contains becomes assimilable in the soil, the experiments reported in this paper were made.

Slag from different localities varies considerably in composition, as will be seen from the following analyses, No. 1 being the average of a number of German samples examined by Fleischer and Hasenclever, and No. 2 a slag from rolling-mills at Willkowitz, in Austrian Silesia:—

	No. 1.	No. 2.
Phosphoric acid	17.5	18.06
Lime	49.6	34.14
Magnesia	4.7	6.26
Ferrous oxide	9.3	23.70
Ferric oxide	4.1	
Alumina	2.0	10.13
Manganese oxide	4.0	0.79
Sulphur, free	0.5	trace
Sulphuric acid	0.2	none
Silicic acid	7.5	3.69

The differences are due doubtless to the description of ores worked and the composition of the basic lining of the converters.

The sample employed by the writer was obtained from Birmingham, and finely ground (for 20-mesh sieve). For each experiment 10 grms. were taken, 100 c.c. of the solvent added, left for two hours, diluted to a litre, the P_2O_5 precipitated by molybdate; precipitate re-dissolved, and estimated as pyrophosphate. The sample contained total phosphoric acid 18.658 per cent = 40.732 per cent $(Ca_3PO_4)_2$.

No.	Solvent.	Per cents dissolved.	
		P_2O_5	$Ca_4(PO_4)_2$
1.	Tap water	1.469	3.206
2.	Peat water	2.236	4.882
3.	Normal sodium carbonate ..	2.556	5.579
4.	Normal sol. acetic acid ..	4.217	9.19
5.	Joulie's formula (ammonium citrate)	6.39	13.949
6.	Ammonium oxalate	11.5	25.104

No. 1.—Tap water was the ordinary Dublin supply, derived from a peaty source, but filtered moderately well.

No. 2 was a decoction obtained by boiling 10 grms. of air-dried peat for one hour, and diluting to 1 litre.

Nos. 3 and 4.—Ordinary normal solutions as used in volumetric analysis.

No. 5 was treated exactly according to the recent directions of Joulie, the solutions having been carefully prepared of correct strength.

No. 6.—In this case the solution was saturated, and the sample boiled in it. The solution was originally intended to test Joulie's theories on the classification of raw phosphates, as given in his book "Engrais Chimiques."

Experiment No. 2 scarcely gives a fair idea of the effects which humus, humic acid, crenic and apocrenic

acids, so called, would exercise on an easily decomposable compound subject to their influence for a long period.

Experiment No. 3 is also a very feeble indication of the effect of large quantities of free carbonic acid for long periods such as are contained in all arable soils. To give a fair idea of this the sample should be subjected for a considerable time to the action of water charged with free carbonic acid.

Experiment No. 4 is very suggestive, probably the most so of the series, in view of the recent investigations on the action of micro-organisms in the soil, and their office of promoting acetic and butyric fermentations therein.

Experiment No. 5 is not less suggestive: the action of citric acid is very decisive. It may be found hereafter that some, perhaps many, of the organic acids of the soil approach in their nature and action citric and tartaric acids.

Of the chemical constitution of those organic compounds, their changes, and the part they play in rendering inorganic substances available for the sustenance of plants, we know little, notwithstanding the great names associated with the subject; still less do we know of the part played by those micro-organisms which recent observations have proved important factors in Nature's operations.

I hope to continue and to amplify those experiments; but, as far as they go, I think they reasonably lead to the opinion that the phosphoric acid in the slag exists in such a state that, when brought into contact with those organic matters, dissociation takes place, and it is rendered easily assimilable by the plants.

I have to thank my young friend Mr. F. J. Richardson for his able assistance in carrying out the experiments.

Laboratory Chemical Manure Works,
Ringsend Docks, Dublin.

ON THE ERROR IN THE NITROMETRIC ASSAY OF VITRIOL.

By THOMAS BAYLEY.

PROF. LUNGE asserts (CHEMICAL NEWS, vol. liii., p. 289) that no error can possibly arise in the nitrometric assay of vitriol, from the presence of iron, since only proto-salts dissolve nitric oxide, and proto-salt cannot exist in presence of nitrous or nitric acid. He also regrets that, before ascribing any such action to iron, I did not try an experiment with nitrous vitriol containing it.

Of course Prof. Lunge is quite correct in saying that only proto-salts of iron form the dark compound with nitric oxide, but, in spite of that, ferric salts contained in vitriol do lead to the absorption of nitric oxide in the nitrometer. If a few drops of a solution of ferric nitrate be mixed in the instrument with pure sulphuric acid the dark colour is obtained, not immediately, but after shaking for a minute or so. And after the experiment the liquid, which previously showed no ferrous reaction, gives a blue colouration with dilute solution of ferricyanide of potassium. Therefore, in contact with mercury and nitric acid, ferric salts are reduced, and it will be interesting to observe whether a similar reaction takes place with other salts than the nitrate.

I have previously stated that "*pur*"—that is, *purified*—sulphuric acid, of the shops, obtained in this neighbourhood, frequently (indeed almost always) gives a colouration with nitre in the nitrometer; but it may or may not be so in other districts, according to the method of purification employed. Having frequently to estimate small fractions of a grain of copper, iron, and other metals per lb. in metallic lead, I have learned not to rely upon the purity of this "*pur*" acid. Acid made from English pyrites from the

coal-measures, containing traces only of copper, is not free from that metal, and requires to be purified for special purposes. Probably the acid gets the copper from the chamber lead, and some at least of the iron in the same way. This acid made from English pyrites is comparatively very free from arsenic, but contains, before rectification, much organic matter. I have found it give the colour reaction of NO and iron (pink to reddish tints) many dozens of times, and cannot understand how Prof. Lunge can have failed to notice this colour when testing his method for impure nitrous vitriol. The matter is still under investigation in my laboratory with a view of finding a way of avoiding the error introduced by iron. I have tried introducing chromate and other oxidising solutions after the shaking, but without the effect of freeing the dissolved gas. But for an oversight a statement of the reaction of mercury upon iron salts would have been contained in my last paper.

With so courteous an opponent as Prof. Lunge I cannot conclude without expressing regret if I have done him an injustice in ascribing the invention of the nitrometer to Davis, who (according to Allen, *J. Chem. Ind.*, March, 1885) claims to have used a similar instrument prior to March, 1878.

The late Mr. Edward Jackson designed a somewhat modified nitrometer, which has the advantage of almost entirely preventing frothing, and of causing rapid separation of the acid and mercury. This instrument is peculiar only in the shape of the graduated tube, which is wide, $\frac{3}{4}$ to 1 inch, and tapers gradually to the tap. The appearance of a tint due to iron is indicated at once with this instrument, the clearing of the acid being very rapid.

Birmingham, June 21, 1886.

CERIUM IN THE HAINSTADT CLAYS.

EXPLANATION.

By Dr. J. R. STROHACKER.

THE *Journal für Praktische Chemie* (No. 9, 1886),* contains an article on the question of the Hainstadt Clays which transgresses the limits of discussion recognised in Europe, and the purport of which is nothing less than that of chemical research, but simply insult. I declare, therefore, hereby, that I maintain point for point my statements in my two memoirs (pp. 132 and 260 of this volume of the *Journal für Prakt. Chemie*), as my analyses were conducted quite carefully.

To meet the points specially raised I remark the following facts:—

1. If the flesh-coloured Hainstadt Clay No. I., in very fine powder is introduced into a concentrated solution of alkali and strongly boiled for two days in a covered iron vessel, all the cerium hydroxide present is dissolved out along with Al_2O_3 and SiO_2 ; Ce_2O_3 is obtained from the solution in the manner described.

2. We may be easily convinced of the solubility of cerium hydroxide in caustic alkali by boiling the precipitate obtained from the hydrochloric extracts of clay No. I. with caustic alkali.

3. Cerium sal-ammoniac, a salt which has long been known, is formed in the nascent state on introducing NH_3 into a solution of Ce_2Cl_6 containing an excess of acid.

4. The pale yellow ferrocyanide solution of Ce_2O_3 obtained from a neutral solution (which I regarded at first as a secondary matter), if the liquid is previously acidulated, takes a blue colour on heating, as the oxidising action of Ce_2O_3 upon hydro-ferrocyanic acid precipitates Prussian blue. This was formerly not observed.

5. The Hainstadt cerium hydroxide has, when freshly precipitated, the greatest resemblance to iron hydroxide. When dried and powdered, however, it forms an orange

yellow—not red-brown—powder. Ce_2O_3 , anhydrous, is a very bright orange-red, whilst Fe_2O_3 , anhydrous, is a blood-red (colcothar). The cerium hydroxide is therefore very distinct from ferric oxide.

6. If, subsequently, a difference is discovered between the Hainstadt and the Swedish cerium, I cannot decide, but it cannot be regarded as Fe, the oxide of which cannot be extracted by caustic alkali.

7. I have extracted the black clay No. II.a never with alkali, but always with HCl, and have always found in it Ce, La, Yt, and in two cases Di; Be, it may be here remarked, is not rare in the minerals of the Odenwald, since the beryl itself is well known to occur in the granites of the district.

8. During the last half year I have obtained from the Hainstadt clays considerable quantities of the salts of lanthanum and yttrium.

9. Other results of eminent analysts have been already announced.

(Signed)

Dr. J. R. STROHACKER.

Frankfort-on-the-Main.

June 16, 1886.

MINOR INVESTIGATIONS.

By L. M. NORTON.

I. Oxidation of Benzol.

THE action of a powerful oxidising agent upon benzol has been occasionally investigated, but the unexpected results obtained in certain cases have hardly attracted the attention they deserve. The formation of benzoic acid by the oxidation of benzol is certainly worthy of notice. Under my direction Mr. J. G. Holder has repeated some previous experiments in this direction, and we have also attempted the oxidation of benzol by some methods not heretofore employed. I give a summary of our experiments. The benzol used in all the experiments boiled between 80.2° and 80.3° , and left no residue at the latter temperature. Our analysis gave figures which corresponded to 92.20 per cent of carbon and 7.70 per cent of hydrogen, while the theory requires 92.30 per cent of carbon and 7.70 per cent of hydrogen. Its perfect freedom from toluol is certain, as long-continued boiling with dilute nitric acid and also with a solution of chromic acid in acetic acid failed to furnish the least trace of benzoic acid. Carius* first investigated the action of binoxide of manganese and sulphuric acid upon benzol and obtained carbonic anhydride, formic acid, benzoic acid, and a phthalic acid. We investigated this method of oxidation under somewhat different conditions with a somewhat different result. Three large flasks were taken and 100 grms. of benzol placed in each. The benzol was carefully cooled, and a mixture of 600 grms. of ordinary pure sulphuric acid and 120 grms. of water slowly added to each flask, all heating being carefully avoided. Next, 100 grms. of powdered MnO_2 were stirred into the mixture in each flask and the mixture then allowed to stand one week, with frequent stirring. The undecomposed benzol was then removed by distillation, the acid nearly neutralised with caustic soda, and evaporated to a small volume, and this liquid treated with ether, which removed an organic acid from the liquid. This acid was then purified. It sublimed without decomposition, agreed in all physical properties with benzoic acid, and furnished barium and calcium salts, which, upon analysis, proved to be the benzoates of barium and calcium. The yield of benzoic acid is small. Carbonic anhydride was the other product of the oxidation which we observed. We were unable to convince ourselves of the presence of formic or phthalic acids.

We next examined the action of peroxide of lead and sulphuric acid upon benzol. By the action of these agents upon benzoic acid Meissner and Shepard* obtained

* *Ann. d. Chim.*, cxlviii., 50.

† *Zeit. f. Chem.*, 1866, 752.

* Also reprinted in the CHEMICAL NEWS, vol. liii., p. 136.

succinic acid and carbonic anhydride. Benzol and PbO_2 were shaken together in a flask and sulphuric acid (sp. gr. 1.56) run in from a drop-funnel. Vigorous action accompanied by frothing takes place in the cold at first, afterwards gentle heating is required to complete the action. After twelve hours heating the undecomposed benzol was removed by distillation, the liquid diluted with water, and filtered. The black residue consisted mostly of PbO_2 and PbSO_4 , and contained no organic acid. The clear liquid was treated with BaCO_3 in excess, filtered, and the filtrate evaporated to dryness. It furnished a barium salt soluble in water, containing 36.50 per cent of barium and corresponding in every respect with benzoate of barium. The free acid from this salt showed all the physical properties of benzoic acid. The yield is much larger than by the action of MnO_2 and H_2SO_4 upon benzol. Carbonic anhydride is formed also in large quantities in the oxidation with PbO_2 and H_2SO_4 .

The statements regarding the action of potassium permanganate upon benzol differ. Berthelot* obtained oxalic acid by the action of alkaline permanganate solution upon benzol, while Adrienz† found formic acid to be the product of the oxidation in an acid solution. The action is certainly very slow. A neutral solution of permanganate failed to attack benzol perceptibly in two weeks, as was proved by the weight of benzol recovered. A strongly acid solution in twelve days oxidised one-fourth of the benzol present, but we could not detect the production of solid or liquid products, while boiling with alkaline permanganate solution for six hours failed to oxidise any of the benzol.

We examined the action of PbO_2 and dilute nitric acid upon benzol. We boiled 50 grms. of benzol, 104 grms. of nitric acid (sp. gr. 1.4), 222 grms. of water, and 30 grms. of lead peroxide with a return cooler for sixty hours. After removal of the undecomposed benzol the dilute acid deposited a crop of crystals which proved to consist of oxalic acid, and no other oxidation-product was observed. Leeds‡ obtained oxalic acid by the oxidation of benzol with ozone and with hydrogen peroxide.

By oxidising benzol with a solution of chromic acid in acetic acid, and also by the action of potassium bichromate and sulphuric acid, we obtained only carbonic anhydride.

II. Action of Isobutyric Acid upon Aniline.

Under my direction Mr. F. L. Bardwell has examined the action of isobutyric acid upon aniline in the presence of zinc chloride. Kahlbaum's isobutyric acid was mixed with pure aniline in the proportion of one molecule of the acid to one molecule of aniline. The liquids were shaken together, but no evidence of chemical action could be detected; a small quantity of anhydrous zinc chloride was then added, whereupon the mixture at once turned to a mass of crystals, and a decided rise in the temperature of the mixture was observed. The crystals were easily soluble in water, and were decomposed by dilute caustic alkalies in the cold and aniline set free. The crystals were doubtless aniline isobutyrate. The crystalline mass obtained by the action described above was placed in a flask, melted, and boiled for from one to two hours beneath a return cooler. At the end of this time the flask was cooled, and contained then a solid mass of crystals. These crystals were washed with dilute hydrochloric acid to remove any undecomposed aniline. They proved to be somewhat soluble in cold water and easily soluble in hot water. Caustic alkalies did not attack them in the cold, but, upon heating, decomposed them, furnishing aniline. The substance was crystallised repeatedly from water and analysed when the melting-point was constant, with the following results:—

0.1535 grm. of substance furnished 0.1130 grm. of H_2O and 0.4165 grm. of CO_2 .

0.9110 grm. furnished 68.14 c.c. of N at 20° and 760 m.m.

* *Compt. Rend.*, lxxiv., 35.

† *Berichte der Deut. Chem. Gesell.*, vi., 443.

‡ *Berichte der Deut. Chem. Gesell.*, xiv., 975.

	Found.	Theory for Isobutyranilide.
H	8.54 per cent.	7.97 per cent.
C	73.99	73.61
N	8.56	8.58

These results show conclusively that the substance is isobutyranilide, isomeric with the butyranilide obtained by Gerhardt,* by the action of a mixture of butyric acid and butyryl chloride upon aniline. Isobutyranilide crystallises from water in colourless prisms which melt at 102.5° without decomposition. It distils also without decomposition. It is somewhat soluble in cold water, easily soluble in hot water, alcohol, and ether. The yield of the anilide is increased by heating the mixture of aniline, isobutyric acid, and zinc chloride in closed tubes at 150°. If aniline and anhydrous isobutyric acid are heated without zinc chloride in a similar manner the anilide can be obtained, but only with difficulty and in small quantities.

Nitric acid acts with great violence upon isobutyranilide, and all attempts to isolate a nitro-compound in a pure condition failed. By the action of bromine upon the anilide a monosubstitution-product was obtained. The anilide was dissolved in cold water, and a current of air charged with bromine water passed through the solution. A heavy precipitate of a yellowish colour separated. This substance was very insoluble in water but readily soluble in hot dilute alcohol. It was purified by repeated treatment with animal charcoal in an alcohol solution, and repeated crystallisations from this solvent, and was finally obtained in colourless needle-shaped crystals.

A bromine estimation furnished the following figures:—0.1569 grm. furnished 0.1220 grm. of AgBr.

	Found.	Theory for $\text{C}_6\text{H}_4\text{BrNHC}_4\text{H}_7\text{O}$.
Br	33.15	33.05

The brom-isobutyranilide melts at 128°, but can be sublimed undecomposed at a somewhat lower temperature. It is soluble in hot water and slightly in cold water, but could not be obtained from water in a crystalline form. It is easily soluble in alcohol. It is unaffected by cold caustic alkali, but hot caustic alkali dissolves it slowly without decomposition. By heating in a closed tube at 125° for several hours with aqueous hydrochloric acid it was decomposed, and furnished the hydrochloride of para-brom-aniline. The free base obtained from this hydrochloric acid salt melted at 67°.† The compound obtained by the action of bromine upon isobutyranilide is, therefore, para-brom-isobutyranilide. The formation of an isomer was not observed. The para-brom-isobutyranilide was treated with a mixture of nitric acid and sulphuric acid, in the manner recommended by Nölting and Collin‡ for the production of nitracetanilide, and furnished a nitro-compound difficult to purify, but which, after repeated crystallisations from alcohol, yielded a yellow crystalline product, melting at 111.5°, containing 36.37 per cent of bromine, and agreeing in all respects with para-brom-orthonitraniline.§

III. The Ethyl-orthotoluidines.

In the course of an investigation upon the products of oxidation of the substituted aromatic amines, Mr. R. L. Chase has prepared under my direction the ethyl-orthotoluidines. These compounds were prepared by Reinhardt and Staedel,|| but they furnished no description of their characteristics.

Ethyl-ortho-toluidine.

Ethyl iodide combines with great readiness with orthotoluidine. If mixed in the proportion of 1 mol. of ethyl iodide to 1 mol. of ortho-toluidine, and allowed to stand

* *Ann. d. Chem.*, lxxxvii., 166.

† Körner, *Jahres. f. Chem.*, 1875, 356.

‡ *Berichte der Deut. Chem. Gesell.*, xvii., 262.

§ Hübner, Retschy, *Berichte d. Deut. Chem. Gesell.*, vi., 796, and Körner, *Jahres. f. Chem.*, 1875, 328.

|| *Berichte d. Deut. Chem. Gesell.*, xvi., 29.

for twelve hours at the ordinary temperature, the mixture becomes a solid crystalline mass consisting of the hydriodide of ethyl-ortho-toluidine. We dissolved this salt in water, in which it is very soluble, and added caustic potash solution, by which a base was set free as an oil. This oil dried over CaCl_2 , and fractionated, furnished a product which boiled at 204° to 206° , and gave the following figures upon analysis:—

		Found.	Theory for Ethyl-ortho-toluidine.
C	79.52	80.00
H	10.03	9.63
N	10.34	10.37

Ethyl-ortho-toluidine is a thin yellowish oil which gradually turns pink upon standing. Our product boiled at 204° to 206° , and remained liquid at -15° . Its specific gravity is 0.5934 at 15.5° compared with water at the same temperature. Its platinum salt separates as an oil, and cannot be obtained in a state of purity owing to the ease with which it is decomposed. It resembles closely the corresponding salt of ethyl paratoluidine.* The hydrochloric acid salt of the base could not be isolated. The hydriodic acid salt separates from water as a jelly, but can be crystallised from alcohol, in which it is less soluble. An iodine estimation in the hydriodide thus purified gave 48.39 per cent of iodine, while the theory requires 48.29 per cent. The acet-compound can be obtained either by the action of acetyl chloride or acetic anhydride upon the base. It is somewhat soluble in water, easily soluble in alcohol and benzol, and separates from these solvents as an oil. It boils between 254° and 264° , and solidifies after long standing.

A nitrogen estimation in the acet-compound gave—

		Found.	Theory for Acetethyl-ortho-toluidine.
N.. ..		8.34 per cent.	7.91 per cent.

The ethyl-ortho-toluidine furnishes, by the method employed by Fischer† for preparing nitroso-methyl-aniline, a nitroso-compound. This compound was purified by distillation with steam, and is a dark brown oil which cannot be distilled alone without decomposition.

A nitrogen estimation gave—

		Found.	Theory for Nitroso-ethyl-ortho-toluidine.
N	16.63	17.05

Diethyl-ortho-toluidine.

When ethyl-ortho-toluidine is heated with an excess of ethyl iodide at 100° for six hours in a closed tube the mixture turns to a mass of white crystals soluble in water. An aqueous solution of this salt treated with caustic potash solution yielded a free base, which was dried over CaCl_2 , fractionated, and proved upon analysis to be diethyl-ortho-toluidine.

		Found.	Theory for Diethyl-ortho-toluidine.
C	80.54	80.98
H	11.06	10.43
N	9.25-9.23	8.58

Diethyl-ortho-toluidine appears to have been first prepared by Baeyer and Caro,‡ but is not described by them. Our product boiled between 203° to 208° , and was a limpid oil, closely resembling the mono-compound. Its hydriodide is less soluble in water than that of ethyl-ortho-toluidine, and crystallises from it in beautiful prisms, which contain 1 mol. of water of crystallisation, and melt at 72° to 73° . An iodine estimation in the anhydrous salt gave 43.78 per cent of iodine, while the theory requires 43.64 per cent. The yield of diethyl-ortho-toluidine was 70 per cent of the theoretical quantity.—*American Chem. Journ.*, vol. vii., No. 2.

* Morley and Abel, *Ann. d. Chem.*, xciii., 311.

† *Ann. d. Chem.*, cxc., 151.

‡ *Berichte d. Deut. Chem. Gesell.*, x., 1262.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Thursday, June 17th, 1886.

Dr. HUGO MÜLLER, F.R.S., President, in the Chair.

(Concluded from vol. liii., p. 306.)

65. "The Estimation of Free Oxygen in Water." By Miss K. I. WILLIAMS and Prof. W. RAMSAY.

The authors have instituted a comparison of Schützenberger's methods of estimating free oxygen in water with each other and with the gasometric method with favourable results. Schützenberger's first method, which consists in adding sodium hyposulphite to a measured quantity of water, using indigo-carmin as an indicator, is stated by him to estimate only half the amount of free oxygen; his second method, in which water containing free oxygen is added to indigo-white, turning it blue, and the amount of oxidised indigo-white is estimated by hyposulphite, was regarded by him as the only accurate one. The authors disprove the assertion, and show that there is a preliminary stage in the first process when colour disappears; but that on standing for some time a blue colour appears, to destroy which permanently requires such an addition of hyposulphite as to make the total amount equal to that employed in operating according to the second method. The proportion of hyposulphite used during the first stage of Method 1 to the total amount used is 3 to 5; but they believe that this proportion was conditioned by the temperature and dilution prevailing during the experiments. It is also shown that hyposulphite of soda reacts to some extent with hydrogen dioxide, thus negating the statements of Schützenberger's of König.

66. "Note as to the Existence of an Allotropic Modification of Nitrogen." By Miss K. I. WILLIAMS and Prof. W. RAMSAY.

Attention was some time ago directed to the existence of an allotropic modification of nitrogen by Mr. J. Stillingfleet Johnson, who stated that an active modification of this element could be prepared by heating a mixture of potassium nitrite and ammonium chloride solutions; and that on passing the evolved gas over heated platinum sponge along with hydrogen, ammonia was formed. The support lately given to this statement by the experiments of Profs. J. J. Thomson and Threlfall has suggested the propriety of testing Johnson's statements by further experiments; the results, however, have been negative. The hydrogen used in the experiments was prepared by the action of chlorhydric acid on granulated zinc. It was collected in a gasholder, and dried by passing it first through sulphuric acid and then over phosphoric anhydride. In preparing the nitrogen 85 grms. of potassium nitrite were dissolved in distilled water, and added to a solution of 53.4 grms. of ammonium chloride; some ammonia and then some crystals of cupric chloride were introduced. On the addition of a sufficient proportion of this latter compound a steady stream of gas came off and was collected in a gasholder. In order to dry it and remove any oxides of nitrogen or ammonia present in the gas, it was first passed through a tube containing pumice-stone soaked in an acid solution of ferrous sulphate, next through a wash-bottle partly filled with sulphuric acid, over pumice-stone soaked with Nessler's reagent, then over pumice-stone soaked with sulphuric acid, and then through a tube filled with phosphoric anhydride. At this point the two streams of gas were brought together by a T-tube, and the mixture passed over heated platinum sponge into bulbs containing chlorhydric acid. At the end of each experiment the contents of the bulbs was washed into an evaporating basin and evaporated over a water-bath; the residue was then dissolved in distilled water, and tested for ammonia with Nessler's reagent.

The first experiment was made with about 4.38 litres of nitrogen prepared at a temperature of about 100°, the result being that the Nessler's reagent was coloured merely a faint yellow. In a second experiment the nitrogen used was evolved at first from the mixed solution by external application of heat, but on adding more cupric chloride the reaction went on alone, and the temperature was lower than in the first experiment. To get accurate results the capacity of the nitrogen gasholder was gauged; when full of water it contained 8.481 litres, equal to 7.7031 litres at 0° C. and 760 m.m. After using the whole of this nitrogen, at the end of the experiment the same tint was obtained as that given by 1.10 c.c. of ammonium chloride solution in 100 c.c. of distilled water with Nessler's reagent, 1 c.c. of the ammonium chloride containing 0.00019107 gm. NH_4Cl , or 0.00005 gm. N. Therefore the amount of "active nitrogen" was only 0.000055 gm. in the 7.7031 litres.

To obtain better results, if possible, during the preparation of the next gasholder full of nitrogen, the flask from which it was evolved was carefully kept below 50° C., the temperature being watched by means of a thermometer placed in the cork of the flask. In this case the ammonia formed produced the same tint with Nessler's reagent as that given by 1.14 c.c. of the standard ammonium chloride solution, proving the presence of only 0.000057 gm. "active nitrogen" in 7.7031 litres. It is evident, therefore, that these experiments fail to corroborate Mr. Johnson's results.

67. "*The Presence of a Reducing Agent, probably Hydrogen Peroxide, in Natural Water.*" By Professor RAMSAY.

Distilled water, as well as ordinary tap water, has a reducing action on potassium permanganate. The amount of the reducing agent is increased by evaporation, even when all possibility of contamination with solid organic impurity is excluded. The amount of reduction is far too great to be ascribed to the nitrites present in the water. The experiments described in the paper show under what circumstances and to what extent this substance—which is probably hydrogen dioxide—is produced. If this supposition be correct, and the active substance in natural water be really hydrogen peroxide, it becomes of importance to ascertain its action on organic impurities contained in many natural waters. Experiments were therefore made quantitatively on the action of dilute solutions of peroxide of hydrogen on urea, and it was found that the urea is slowly oxidised on standing: the rate of this action has also been measured. (Comp. H. B. Dixon, *Chem. Soc. Trans.*, 1886, p. 108.)

68. "*Evaporation and Dissociation. Part IV. A Study of the Thermal Properties of Acetic Acid.*" By W. RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

This paper contains a record of measurements of the relative density of liquid acetic acid at 13.11° (water at 4° = 1.0), the number obtained being 1.05682; its expansion up to a temperature of 280°, at which the volume of 1 gm. is 1.5172 c.c.; its vapour-pressures, which reach 24,600 m.m. at 280°; and the density of its saturated and unsaturated vapour at different temperatures and pressures. The minimum value of the density of the saturated vapour is at 150°, and is equal to 50.06 ($H = 1.0$); it increases both with rise and with fall of temperature. The values of $\frac{dp}{dt}$ have also been calculated, and from them and from the other data the heats of vapourisation have been deduced. Here, again, there is a maximum value at 110.6; the latent heat at this point is 92.8° C., and decreases both with rise and fall of temperature. Diagrams are appended contrasting the behaviour of acetic acid with that of alcohol and of ether.

69. "*Note on the Vapour-Densities of Chloral Ethyl-Alcoholate.*" By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

This paper contains an account of determinations of

the densities of the saturated and unsaturated vapour of chloral ethyl-alcoholate. The amount of dissociation is always very great, the percentage number of molecules decomposed being never less than 75. Owing to the very small variation of vapour-density under different conditions of pressure and temperature, to the impossibility of obtaining very concordant results with such a substance, and to the fact—noticed to a smaller extent with acetic acid—that on decreasing the volume condensation begins before the pressure has reached its maximum, it is impossible to draw any very definite conclusion regarding the relation of the density of the saturated vapour of this body to the temperature, but it may be stated that a rise in the density of the saturated vapour with fall of temperature could not be detected. The density of the unsaturated vapour diminishes with rise of temperature at constant pressure, and with fall of pressure at constant temperature.

70. "*The Nature of Liquids as shown by a Study of the Thermal Properties of Stable and of Dissociable Bodies.*" By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

After Deville advanced the theory of dissociation, its opponents endeavoured to explain the abnormality of the vapour-density of unstable bodies by ascribing it to a deviation from Avogadro's law supposed to occur in many liquids at temperatures and pressures near their condensation points. No complete research having been made to compare the behaviour of stable and of dissociable bodies in this respect, the authors have investigated the thermal properties of alcohol, ether, acetic acid, and chloral alcoholate. In all cases they have found abnormality at high pressures. But whereas with alcohol and with ether the density of the saturated vapour becomes and remains normal below certain temperatures, with acetic acid the density when at its lowest is abnormally high and increases with fall as well as with rise of temperature. The two theories alluded to above, by which attempts have been made to explain this abnormal density, are (1) that the gaseous molecules exercising attraction on one another are thereby drawn closer together, and (2) that gaseous molecules combine to form more complex molecules such as are by many supposed to exist in liquids. It appears to the authors inconceivable that this effect should be produced by the same cause under conditions so totally different: for at low temperatures the stability of a saturated vapour is greater while the molecules are necessarily further apart; and at high temperatures, owing to the high pressure, the molecules are in closer proximity, while the stability is necessarily decreased. With acetic acid it appears therefore that the abnormality at high temperatures is due to a physical cause, common to all liquids, but at low temperatures must be ascribed to some sort of chemical combination between the gaseous molecules.

71. "*The Electromotive Forces Developed during the Combination of Cadmium and Iodine in Presence of Water.*" By A. P. LAURIE, B.A., B.Sc.

The author has determined by means of a Thomson electrometer the electromotive forces of cells consisting of a cadmium and a platinum plate immersed in a solution of cadmium iodide containing free iodine. In one set of experiments, the amount of cadmium iodide in solution was constant and the amount of iodine was varied; in another the amount of cadmium iodide varied, the solution being in each case saturated with iodine; in a third, a constant amount of iodine but varying amounts of cadmium iodide were used. The result of the experiments is to show that if cadmium and water containing cadmium iodide and free iodine are brought together, a considerable electromotive force is developed, which steadily falls. This depends on the facts (1) that as the free iodine is diminished, the electromotive force falls gradually at first, but more rapidly the less iodine there is present; (2) that as the cadmium iodide solution increases in strength, the electromotive force falls off very rapidly while very small quantities of the salt are present, but more and more slowly as the amount

of salt present becomes considerable. In both cases the change may be represented by a continuous curve. The actual values are given in the paper.

72. "*Detection and Estimation of Iodine, Bromine, and Chlorine.*" By M. DECHAN.

To separate iodine from a mixture of chloride, bromide, and iodide, the author distils with a concentrated solution of potassium bichromate (40 grms. $K_2Cr_2O_7$ to 100 c.c. water); on repeating the distillation, after adding a small quantity of sulphuric acid, the bromine only passes over provided that the solution be not too concentrated. The apparatus is therefore so arranged that by means of a stopcock funnel water may be added whenever necessary. The following results are quoted:—

Iodine.		Bromine.		Chlorine.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0.01443	0.01441	0.0126	0.01254	0.0123	0.0122
0.0288	0.02833	0.0252	0.0250	0.056	—
0.0576	0.05628	0.0504	0.05009	0.194	—

73. "*The Analysis of Alloys and Minerals containing the Heavy Metals, Selenium, Tellurium, &c.*" By THOMAS BAYLEY.

The metals precipitable as sulphides are commonly divided into the two groups of those forming sulphides insoluble in alkaline sulphides, and those whose sulphides are soluble; the method of extraction with an alkaline sulphide is often applied in qualitative but less often in quantitative analysis, owing to the difficulty of completely removing the soluble sulphides when once they have been precipitated in admixture with the other sulphides. Instead of precipitating both classes together, it is better, the author finds, to prevent the precipitation of the thio-salt forming elements altogether, experience having shown that the process conducted on this principle is at once accurate and very easy of execution. The process recommended consists in passing sulphuretted hydrogen into a boiling solution containing the substance together with citric and tartaric acids and caustic soda.

NOTICES OF BOOKS.

Oils and Varnishes. Edited by JAMES CAMERON, F.I.C. London: J. and A. Churchill.

THIS work forms one of "Churchill's Technological Handbooks," and deals with an important subject concerning which correct practical information is not easily to be met with.

From the preface, Cooley's "Cyclopædia" appears to have served as the basis of the present volume, to which has been added information derived from more recent sources.

The author discusses, in his first chapter, the chemistry of oils, considering the animal and vegetable fixed oils, followed by the volatile oils, fatty and essential. Under animal oils we find mention of "insect oils," which are certainly, so far, more curious than industrially or commercially important. Then follow in succession the empyreumatic oils, the waxes, and the mineral oils. Under the last head we find instructions for the storage of petroleum, and notes on the construction and management of petroleum lamps.

The eighth chapter discusses the purification, bleaching, and refining of oils. Here we note that one of the best processes—probably the best as far as medicinal oils are concerned—has been accidentally overlooked. Concerning this process we may mention the interesting fact that it was lately purchased by a certain firm for several hundred pounds, as a secret, although it was at the time in print and open to all the world.

The chapter on testing oils is the most extensive in the

book, and relates to their purity, lubricating properties, and illuminating efficiency. Here we find a Miss Kate Crane credited with the discovery "that the cohesion figures of oils may be usefully employed as tests of the identity and purity of oils." The authority quoted is the *American Journal of Pharmacy*, iv., p. 406. Unfortunately the date of this communication is not given. This is an important point as regards priority, since in the *CHEMICAL NEWS* for 1868 (vol. xviii., p. 299) is to be seen a paper, by Dr. R. Carter Moffat, entitled "Oleography: being a Process for the Utilisation of Tomlinson's Cohesion Figures." Miss Crane, as quoted in the work before us, makes no reference either to Dr. Moffat or Mr. Tomlinson, nor does Dr. Moffat refer to her researches. Thus, pending the date of vol. iv. of the *American Journal of Pharmacy* being ascertained, we are unable to decide who is the "first and true inventor."

The spectroscopic examination of oils, proposed by Doumer, is briefly described, but the author expresses no opinion as to its trustworthiness. At the conclusion of this chapter the author discusses photometry and the "standards of light," which he justifiably regards as by no means perfect. Concerning the cost of different sources of light, he shows that taking petroleum at 1s. per gallon, and coal-gas at 3s. 6d. per 1000 cubic feet, "a given quantity of light from the former costs only about half what it does when obtained from the latter, with the additional advantage that properly purified petroleum oil in burning does not produce sulphur compounds."

The concluding chapters are devoted to resins and varnishes.

The entire work is replete with valuable information, and will prove a great convenience to persons connected with the trades and manufactures interested.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cii., No. 24, June 15, 1886.

Absorption-Spectra of Oxygen.—J. Jansen.—This paper will be inserted in full.

Remarks on the Decomposition of Ammoniacal Salts by Metallic Bases and Oxides.—M. Berthelot.—Berthelot explains the preparation of ammoniacal gas by its volatility opposed to the fixity of the alkaline bases. This explanation is exact but insufficient, since it does not explain the partial character of the reaction of most metallic oxides. Neither does it render intelligible what takes place in presence of water, in conditions where the ammonia remains dissolved; nor why lime, baryta, and strontia dissolve in solutions of ammonium chloride, whilst ammonia does not precipitate calcium, barium, and strontium chloride. Even in the case of soda in presence of an excess of water, the theory of Berthelot would involve the distribution of the acid between the soda and the ammonia in a proportion determined by their capacity of saturation and their quantity. But the author has proved by thermic determinations that soda displaces ammonia in dilute solutions entirely or approximately, independent of volatility and whatever may be the relative proportions. Lime acts in the same manner, contrary to the ancient principle of insolubility. It is, therefore, not surprising that in default of water ammoniacal gas escapes; its displacement not being really due to its volatility, but to a previous and independent chemical reaction.

Ammonia in Soils.—Th. Schloësing.—The author raises the question: Are the quantities of ammonia con-

tained in vegetable soils comprised, generally, between 0 and 20 m.g., conformably to the determinations of M. Boussingault, of the author, and of other analysts, or are they from 78 to 118 m.g., as found by MM. Berthelot and André? The relations between the soil and the atmosphere, concerning the exchange of ammonia, depend upon the solution arrived at.

Lavoisier and the Commission of Weights and Measures.—E. Grimaux.—Lavoisier, at the time of his arrest, was a member of the Commission of Weights and Measures. From an unpublished document which has fallen into the hands of M. Grimaux it appears that on Dec. 19, 1793, the Commission addressed to the Committee of Public Safety a formal request for his liberation as necessary for the verification of the numerous standards of weights and measures with which the Commission was then engaged, researches on the weights and the expansion of metals being in particular interrupted by his absence. This document is signed by Borda as president and Haüz as secretary, and is entirely in the handwriting of the latter. The reply was curt and significant: "The Committee of Public Safety, considering that the citizen Lavoisier is entered upon the list of the ex-Fermiers-generaux, arrested in execution of the decree of the National Convention (Nov. 24, 1793), passes to the order of the day." In proof that this attempt on the part of the Commission to save their illustrious colleague was not free from danger, it appears that a few days later the Committee of Public Safety decreed that not only Lavoisier, but Borda, Laplace, Coulomb, Brisson, and Delambre should cease from that date (Dec. 26) to be members of the Commission of Weights and Measures."

Spectroscopic Observations on Fabry's Comet.—L. Cruls.—The three bands characteristic of the compounds of carbon were distinctly seen.

Law of the Electro-conductivity of Saline Solutions of Mean Concentration.—E. Bouty.—As the conclusion of a mathematical investigation the author states that the excess of the specific resistance of a salt beyond its limit value is almost inversely as the mean distance of its molecules.

Relation between the Coefficient of Self-induction and the Magnetic Action of an Electro-magnet.—M. Ledebour.—The curves obtained are shown in diagrams.

On Phosphorus Pentasulphide.—F. Isambert.—This compound is obtained by exposing to the rays of the sun a mixture of sulphur and phosphorus dissolved in carbon disulphide. A yellowish white powder is deposited, which in about a year crystallises as a confused mass. It ignited it burns in the air, giving off sulphurous and phosphoric acids. If heated it melts, and at high temperatures it distils with great difficulty.

Principle of Equivalence in the Phenomena of Chemical Equilibria.—H. Le Chatelier.—The experimental law which serves as the basis of rational mechanics: "Two forces equal to a third are equal among themselves and reciprocally," is exact also in the case of chemical equilibria. But in view of such an application it is preferable to modify the statement by suppressing the notion of force, the source of continual equivocations when we are speaking of phenomena which cannot be produced by direct muscular effort. It will then take the following form:—"In every phenomenon of equilibrium two material systems, which are equivalent as regards a third, *i.e.*, which can singly form an equilibrium to it, will remain equivalent as regards any other system to which they are opposed, and if opposable to each other they form a mutual equilibrium. The author applies this principle to evaporation, to dissociation, to solubility, the decomposition of salts by water, the double decomposition of salts, and the action of presence.

Sodium Mono-orthophosphate and Mono-arsenate.—A. Joly and H. Dufet.—This paper relates principally to the crystalline forms of the two salts.

A Compound of Methylic Alcohol and Anhydrous Baryta.—M. de Forcrand.—The author has obtained a compound of the formula $2C_2H_5O_2, 3BaO$.

On Butyl Monochloracetate.—G. Gehring.—This compound is a colourless, very mobile liquid, of a pleasant fruity odour and a burning taste. It dissolves in alcohol in all proportions; in water it is very sparingly soluble. It is slowly saponified by potash lye. Its specific gravity at 0° is 1.103.

Compounds of Water and Alums.—E. J. Maumené.—The alums are considered as combined with one and the same quantity of water, 24 mols. But a careful analysis shows that in potash-alum the water amounts to 28.73, almost 5 mols. in excess of the classical formula.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. 4th Série. Vol. i., No. 5, May, 1886.

Report Delivered by A. E. Bérard on behalf of the Committee of Chemical Arts on Amagat's "Differential Ebullioscope."—This instrument cannot be intelligibly described without the accompanying cut.

Treatment of Certain Mineral Phosphates of the Type known under the Name of "Redonda."—W. J. Williams.—Taken from the *Journal of the Society of Chemical Industry*.

MISCELLANEOUS.

Result of the Nitrate of Soda Prize.—Carrying out the scheme of prizes offered by the Committee of the Saltpetre Producers' Association (Comité Salitéro at Iquique, Chili), for the best popular Essay treating of the "Importance of Nitrate of Soda as a Manure, and the Best Mode of its Application," the Judges—Prof. L. Grandeau, Nancy (France); Prof. Adolf. Mayer, Wageningen (Holland); Prof. A. Petermann, Gembloux (Belgium); Prof. G. Thoms, Riga (Russia); Prof. Paul Wagner, Darmstadt (Germany); Mr. R. Warrington, Rothamsted (England)—have examined the Essays sent in, namely, 13 German, 13 English, 4 French, and have made the following awards:—1. To the Essay with the motto "Grau, theurer Freund, ist alle Theorie" a partial prize of £350 (7000 marks). 2. To the Essay with the motto "Pour pratiquer l'agriculture. . . ." a partial prize of £150 (3000 marks). On opening the accompanying envelopes the author of the First Essay was found to be Dr. A. Stutzer, Principal of the Agricultural Experimental Station at Bonn; and the author of the Second Essay, M. A. Damseaux, Professor in the Agricultural Academy at Gembloux. It should be remembered that Essays competing for the second part of the prize offered—namely, £500 for the best Essay treating of the same subject, on the basis of *new, personal, experimental investigations*—must be sent to one of the above-named Judges on or before January 1st, 1887.—On behalf of the Comité Salitéro, P. WAGNER.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Royal Institution, 5. General Monthly Meeting.
FRIDAY, 9th.—Quekett, 8.

BISULPHIDE OF CARBON, CHLORIDE OF SULPHUR.

FRANKLIN BARROW,
CLAYTON
Near MANCHESTER.

THE CHEMICAL NEWS.

VOL. LIV. No. 1389.

ON SOME NEW ELEMENTS IN GADOLINITE AND SAMARSKITE,* DETECTED SPECTROSCOPICALLY.

By WILLIAM CROOKES, F.R.S., V.P.C.S.

THE recent discovery by my distinguished friend M. de Boisbaudran† of the existence of a new element which he calls Dysprosium makes it unadvisable on my part, as a fellow investigator in spectroscopic research, to delay any longer the announcement of some of the results I have obtained during the fractionations of the samarskite and gadolinite earths.

I will first take the earths which give absorption spectra when their solutions are examined by transmitted light. These occur chiefly at the higher end, beginning with didymium and proceeding, through samarium, holmium, &c., to erbium, which is one of the least basic. The earths which give phosphorescent spectra chiefly occur at the lower end, but each group overlaps the other; for instance yttria occurs above erbia.

One of the highest of the absorption-spectrum earths is didymia. The spectrum of didymium, as generally met with, is well known, and is given in my paper on "Radiant Matter Spectroscopy: Part 2, Samarium." (par. 135).

It has long been suspected that didymium is not a simple body, and in June, 1885, Dr. Auer v. Welsbach announced that by a series of many hundred fractional crystallisations he had succeeded in splitting up didymium into two new elements, one giving leek-green salts and the other rose-red salts. The green body he called Praseodymium and the rose-red Neodymium. I have not found that my method of fractionation gives a decomposition similar to this; probably didymium will be found to split up in more than one direction, according to the method adopted; but by pushing the fractionations at the didymium end of the series to a considerable extent, a change gradually comes over the spectrum. At the lower end the earth gives an absorption spectrum such as is usually attributed to didymium, but with no trace of some of the bands in the blue end, the one at λ 443 being especially noticeable by its absence. The intermediate earths give the old didymium spectrum, the relative intensities of some of the bands varying according to the position of the earth in the series, the band 443 becoming visible as the higher end is approached. The highest fractions of all give the band 443 one of the most prominent in the spectrum, being accompanied by other fainter bands which are absent in the lowest didymium spectrum.

In my note-book, under date 3rd March, 1886, after discussing the absorption spectrum given by one of my earths rather low down in the series (fraction -3), and comparing coincidences of the lines with those given by holmia, erbia, didymia, thulia, and samaria, I remark "the big blue line (λ 451.5) is still unclaimed." In ignorance that my friend M. de Boisbaudran was on the same track, and running me somewhat close, I deferred further examination of these fractions till a few months longer work had been performed on them, when I hoped to get fuller evidences of a new absorption spectrum. This big line in the blue, λ 451.5, now proves to be the characteristic line of dysprosium. This line does not occur in didymium. The next strongest line, λ 475, is coincident with a very faint line in the old didymium spectrum, and it also falls within a broad band of samarium. M. de Bois-

baudran says that this line is not due either to didymium, erbium, or samarium; as it follows the same variations of intensity as the other lines of dysprosium he considers it due to the same element.

The earth (-3), which I have already mentioned as giving the broad black band (451.5) of dysprosium, shows this band wider (and therefore presumably stronger) than in the spectrum given by M. de Boisbaudran, without the slightest trace of the band 475, which, according to M. de Boisbaudran, should be wider and almost as dense as the band 451.5. It is obvious therefore that the element giving the band 475 cannot be the same as the one causing the band 451.5, and if the body giving the strongest of these is called dysprosium another name must be chosen for the element which gives rise to the absorption-band 475.

And now comes the question: What is the origin of band 475? In remarks made on the band 443 I mentioned that it is accompanied by other fainter lines. One of these occurs at 475, and therefore I was prepared to connect these bands as being due to one and the same element; but M. de Boisbaudran, in his description of the spectrum of dysprosium, has shown that band 475 can be obtained strong in the absence of 443. The bands 443 and 475 therefore are not caused either by didymium, dysprosium, or any hitherto identified element; consequently each must be regarded as characteristic of a new body.

I now come to a branch of the subject which promises to yield results even more fruitful than those given by the examination of absorption spectra: I refer to the spectra yielded by some of the earths when phosphoresced *in vacuo*. This method has been so fully explained before the Royal Society, in my papers on "Radiant Matter Spectroscopy," that I need not repeat it.

In my Bakerian Lecture on Yttrium* I described the phosphorescent spectrum of this earth, and gave a drawing of it. In the Samarium paper† I gave a similar description and drawing of the samarium spectrum, and also described and illustrated some anomalous results obtained when yttria and samaria were mixed together. Under the conditions described in the paper a sharp and brilliant orange line made its appearance, which at that time seemed as if it belonged to the samarium spectrum, and was only developed in greater intensity by the presence of yttria. This explanation, however, did not satisfy me, and I called the line (λ 609 = $\frac{1}{\lambda_2}$ 2693) "the anomalous line," intending to return to it at the first opportunity.‡ I have since further investigated the occurrence of this line, with more than usual good fortune in the extent and importance of the new facts thereby disclosed.

Systematic fractionation was carried on with the portions of the general series giving the strongest appearance of line 609, and it soon became apparent that the line closely followed samarium. The presence of yttria was not necessary to bring it out, although by deadening the brightness of the other bands it was useful, not seeming to affect the line 609. Several circumstances, however, tended to show that although line 609 accompanied samarium with the utmost pertinacity, it was not so integral a part of its spectrum as the other red, green, and orange lines. For instance, the chemical as well as physical behaviour of these line-forming bodies was different. On closely comparing the spectra of specimens of samaria from different sources, line 609 varied much in intensity, in some cases being strong and in others almost absent; the addition of yttria was found to greatly deaden the red, orange, and green lines of samarium while yttria had little or no effect on

* *Phil. Trans.*, Part 3, 1883.

† *Ibid.*, Part 2, 1885.

‡ In paragraph 146, page 713, of the Samarium paper already quoted, speaking of this line, I said it was "so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture."

* A Paper read before the Royal Society, June 10th, 1886.

† *Comptes Rendus*, cii., p. 1003, May 3, 1886.

the line 609; again, a little lime entirely suppressed line 609, while it brought out the samarium lines with increased vigour. Finally, attempts to separate line 609 from samarium and those portions of the samarskite earths in which it chiefly concentrated resulted in sufficient success to show me that, given time enough and an almost inexhaustible supply of material, a separation would not be difficult.

But what was then practically impossible to me, restricted with limited time and means, Nature has succeeded in effecting in the most perfect manner. I had been working on samarskite, and many observations had led me to think that the proportion of band-forming constituents varied slightly in the same earth from different minerals. Amongst others, gadolinite showed indications of such a differentiation, and therefore I continued the work on this mineral. Very few fractionations were necessary to show that the body giving line 609 was not present in the gadolinite earths; no admixtures of yttria and samaria from this source giving a trace of it. It follows therefore that the body whose phosphorescent spectrum gives line 609 occurs in samarskite, but not in gadolinite; thus it cannot be due to samarium, yttrium, or a mixture of these two elements; the only other probable alternative is that the source of this line is a new element.

Chemical fractionation is very similar to the formation of a spectrum with a very wide slit and a succession of shallow prisms. The centre portion remains unchanged for a long time, and the only approach to purity at first will be at the two ends, while a considerable series of operations is needed to produce an appreciable change in the centre.

During the later fractionations of the gadolinite earths another set of facts, formerly only suspected, have assumed consistent form. The spectrum bands which hitherto I had thought belonged to yttria soon began to vary in intensity among themselves, and continued fractionating increased the differences first observed. It would exceed the limits of a preliminary note were I to enter into details respecting the chemical and physical reasons which lead me to the definite conclusions I now bring before this Society. More than 2000 fractionations have been performed to settle this single point. I will content myself with stating the results. The earth hitherto called yttria appears to be a highly complex body, capable of being dissociated into several simpler substances, each of which gives a phosphorescent spectrum of great simplicity, consisting for the most part of only one line.

Taking the constituents in order of approximate basicity (the chemical analogue of refrangibility) the lowest earthy constituent gives a violet band (χ 456), which I have reason to believe belongs to ytterbia. Next comes a deep blue band (λ 482); then the strong citron band (λ 574), which has increased in sharpness till it deserves to be called a line; then come a close pair of greenish blue lines (λ 549 and λ 541, mean 545); then a red band (λ 619), then a deep red band (λ 647), next a yellow band (λ 597), then another green line (λ 564); this (in samarskite yttria) is followed by the orange line (λ 609) of which I have already spoken; and finally, the three samarium bands remain at the highest part of the series. These for the present I do not touch, having my hands fully occupied with the more easily resolvable earths.

In the *Comptes Rendus* for April 19th, 1886, M. de Boisbaudran announces to the Academy that M. de Marignac, the discoverer of Y_a , had selected for it the name Gadolinium. In February last I gave a short note on the earth Y_a ,* in which I described its phosphorescent spectrum (agreeing exactly with that given by Y_a of M. de Marignac's preparation). Referring to my paper it will be seen that Y_a is composed of the following band-forming bodies:—(541, 549), (564), (597), (609), (619), together with a little samarium. Calling the samarium an impurity, it is thus seen that gadolinium is composed of at least four simpler

bodies. The pair of green lines (λ 541 and λ 549, mean 545), being the strongest feature in its spectrum, may be taken as characteristic of gadolinium: the other lines are due to other bodies.

It is by a method of his own, differing from mine, that M. de Boisbaudran has obtained phosphorescent spectra of some of these earths. He takes the induction spark between the surface of a strong and acid solution of the metallic chloride, and a clean platinum wire a few millims. above it. The platinum wire is kept negative and the solution positive; it is then observed that in many cases a thin layer of fluorescent light is seen at the surface of the liquid. This layer gives a spectrum of nebulous bands. For the sake of brevity I will adopt M. de Boisbaudran's term, and call this process the *method of reversion* (the direction of the spark being reversed). As this method is entirely different to the one I adopt, it is not surprising that the results also are different. Experimenting in this way M. de Boisbaudran has obtained, among others, two bands (λ 573 and λ 543.2), which he considers to be caused by two elements, named respectively Z_a and Z_β , and which he considers new, at all events if we except terbium and possibly the elements of what was formerly called holmium. His method fails to show any spectrum in solutions of yttria which by my method give the yttria bands with the greatest brilliancy; while conversely his method shows a fluorescent spectrum in solutions of earths separated as widely as possible from yttria, chemically as well as spectroscopically. My experiments on both these methods tend to the conclusion that our bands are not due to the same cause, although M. de Boisbaudran's experiments have led him to the opposite conclusion. The band of Z_β (543) falls between the double green band of gadolinium (549 and 541), and the band of Z_a (573) would come very near the citron line (574).

A hitherto unrecognised band in the spectrum by absorption or phosphorescence is not of itself definite proof of a new element, but if it is supported by chemical facts such as I have brought forward there is sufficient *prima facie* evidence that a new element is present. Until, however, the new earths are separated in sufficient purity to enable their atomic weights to be approximately determined, and their chemical and physical properties observed, I think it is more prudent to regard them as elements on probation. I should therefore prefer to designate them provisionally by the mean wave-length of the dominant band. In this I am following the plan adopted by astronomers in naming the minor planets, which are known by a number encircled by a line. If, however, for the sake of easier discussion among chemists a definite name is thought more convenient I will follow the plan frequently adopted in such cases, and provisionally name these bodies as shown in the Table. (See next page).

The initial letters D, S, and G recall the origin of the earths respectively from Didymium, Samarskite, and Gadolinite.

The radiant-matter test for these phosphorescing bodies proves itself every day more and more valuable, as one of the most far-searching and trustworthy tools ever placed in the hands of the experimental chemist. It is an exquisitely delicate test capable of being applied to bodies which have been approximately separated, but not yet completely isolated, by chemical means; its delicacy is unsurpassed even in the region of spectrum analysis; its economy is great, inasmuch as the test involves no destruction of the specimen; its convenience is such that any given test is always available for future reference, and the quantity of material is limited solely by the power of the human eye to see the body under examination. Beyond all these in importance is its trustworthiness. I should be exceeding the legitimate inference from experience were I to say that the test is infallible; but this I may say—during the five years in which this test has been in daily use in my laboratory, I have never once been led to view its indications with suspicion. Anoma-

* *Proceedings of the Royal Society*, No. 243, February, 1886.

Position of lines in the spectrum.	Scale of spectrosc.	Mean wave-length of line or band.	$\frac{1}{\lambda^2}$	Provisional name.	Probability.
Absorption bands in violet } and blue.. .. . }	8.2707 8.828	443 475	5096 4432	Da Sβ	New. New.
Bright lines in—					
Violet	8.515	456	4809	Sγ	Ytterbium.
Deep blue	8.931	482	4304	Gα	New.
Greenish blue (mean of) a close pair) }	9.650	545	3367	Gβ	Gadolinium, or Zβ.
Green	9.812	564	3144	Gγ	New.
Citron	9.890	574	3035	Gδ	New, or Za.
Yellow	10.050	597	2806	Gε	New.
Orange	10.129	609	2693	Sδ	New.
Red.. .. .	10.185	619	2611	Gζ	New.
Deep red	10.338	647	2389	Gη	New.

lies and apparent contradictions have cropped up in plenty, but a little more experiment has always shown that the anomalies were but finger-posts pointing to fresh paths of discovery, and the contradictions were due to my own erroneous interpretation of the facts before me.

ON THE FLUORESCENCE FORMERLY ATTRIBUTED TO YTTRIA.

By M. LECOQ DE BOISBAUDRAN.

THE Academy doubtless remembers the discussion which has taken place before it, between Mr. Crookes and myself, on the subject of the origin of the fluorescent bands which my learned English friend attributes to yttria, while I have considered them due to impurities from which it has only been very difficult to purify true yttria.

I have shown* that purified yttria (characterised by the electric spectrum obtained with its hydrochloric solution) no longer gives rise to fluorescent phenomena, not only when its hydrochloric solution is treated by the method of *reversement*, but also when its anhydrous sulphate is submitted to the action of the electric discharge *in vacuo*, by the beautiful process discovered by Mr. Crookes.

By recently recognising the complexity of old yttria,† and by announcing the existence of new elements characterised by the fluorescent bands formerly attributed to yttria, it appears to me, therefore, that Mr. Crookes has in reality completely come round to the opinion I have always maintained; although he has not referred to this opinion (doubtless through inadvertence) in the article which he caused to appear in the English journal *Nature* on the 17th of June last.‡

According to the latest work of Mr. Crookes, the fluorescent bands of the old yttria, although they are not due to yttria properly so called, have really origins different from those of my fluorescences, Za and Zβ, obtained by *reversement*;—fluorescence Za and Zβ, which, I think, have the same chemical origin as Mr. Crookes's fluorescences *in vacuo*.

In the hope of contributing to clear up this question, I have made the following experiments:—

After a long series of careful fractionations I have obtained a terbia § which gives, by *reversement*, a magnificent fluorescent spectrum, composed of all the bands Zβ|| with only a faint trace of the yellow band of Za.

* *Comptes Rendus*, p. 591, Sept. 14, 1885, and CHEMICAL NEWS, vol. lii., p. 299.

† *Nature* (English), June 17, 1886, p. 160-62.

‡ The article in *Nature*, to which M. de Boisbaudran refers, was only an abstract of my Royal Society paper. On referring to the complete paper, which immediately precedes this article, it will be seen that, whilst I have by no means come round to M. de Boisbaudran's opinion, I have not failed in my duty to give the fullest credit to M. de Boisbaudran for his beautiful discoveries.—W. CROOKES.

§ The fluorescence of Zβ, by *reversement*, is at its maximum intensity in the terbias most coloured reddish brown; Zβ therefore appears to be identical with Tr, or, at least there is as yet no proof against this identity.

|| *Comptes Rendus*, p. 899, April 19, 1886.

I introduced a little of this terbia into purified yttria, which no longer gave *in vacuo* Mr. Crookes's old fluorescence, or, at least, only showed an insignificant trace of the citron band. The anhydrous sulphate of this mixture (yttria soiled by a little terbia) showed *in vacuo* a fine fluorescence, in which glowed the two green bands of the drawing given by Mr. Crookes as that of old yttria; the relative intensities of these bands, their width, &c., exactly conform to this drawing. In short, these are Mr. Crookes's two green bands obtained with a trace of terbia which only gave by *reversement* one single wide band. In this experiment the spectrum of samarium was well developed,* but the whole of the spectrum of Zβ was very faint, except the two green bands of which I have just spoken. The colour of the fluorescence, to the naked eye, was of a very clear orange-yellow colour.

Having repeated the experiment with lime instead of yttria, I obtained *in vacuo* a magnificent fluorescence of a beautiful green colour, and more brilliant than that realised by yttria, mixed with terbia. This time the green band was not doubled. The other bands of Zβ were good. The fluorescence of Za (feeble with terbia by *reversement*) was well developed, and comprised the yellow and blue bands. On the contrary, the two green rays of Mr. Crookes could not be seen, and the samarium bands were weak.

I then made a similar double experiment, starting with an earth giving by *reversement* a fine spectrum of Za and a more feeble one of Zβ; this earth contains a notable quantity of erbia and holmia.

With purified yttria, mixed with a small quantity of the earth in question, the fluorescence *in vacuo* gave a very fine citron band, apparently identical with that described by Mr. Crookes, that is to say, a nebulous band on which appears a very narrow ray, with sharp edges, which is not seen in this form in the spectrum obtained by *reversement*. The green band is fainter than the citron band, but it is double, as in Mr. Crookes's drawing. The colour of the fluorescence, to the naked eye, is much whiter than with yttria and the brightness is superior.

Two principal explanations appear to me possible for these observations:—

1. The citron and double green bands of Mr. Crookes are no other than my *reversement* bands of Za and Zβ, modified in their structure by the nature of the solid body which serves, as it were, as a diluent for the active matter.

2. The citron and double green bands have origins different from those of my Za and Zβ bands, and we therefore must admit the singular fact that Mr. Crookes's bands are produced, to the exclusion of bands Za and Zβ, in the presence of excess of yttria, while the reverse takes place in the presence of lime.

Mr. Crookes, in *Nature*, appears to attribute to gadolinium the double green band; this led me to try the above experiments.

* My terbia, the concentrated hydrochloric solution of which no longer gave, in a thickness of about 15 m.m., an appreciable trace of the absorption bands of samarium, evidently still contains a very small quantity of this body, as well as of gadolinium, the electric spectrum of which has also ceased to be discernible.

With yttria the bands of Sm and Gd are produced almost alone. With lime the bands of Z α and Z β appear to the complete exclusion of the two green bands of gadolinium, and the almost complete exclusion of those of samarium.*

It will be seen that there is still much of interest to be done on this subject.—*Comptes Rendus*, vol. cii., pp. 1536—9. June 28, 1886.

DECOMPOSITION OF AMMONIA BY ELECTROLYSIS.

A LECTURE EXPERIMENT.

By the Rev. A. IRVING.

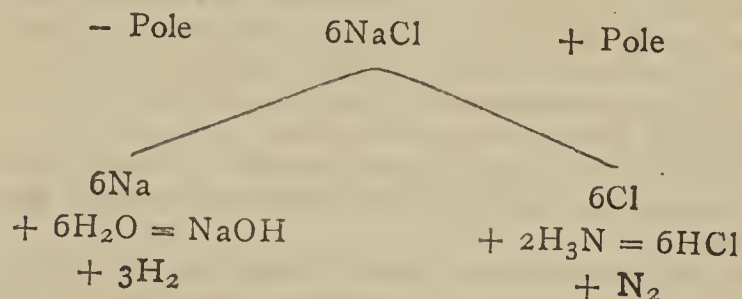
At the present moment, when electrolytic processes are receiving so much attention, it is worth while, perhaps, to draw attention to the following experimental demonstration of the proportion in which hydrogen and nitrogen gases separate out from ammonia. So far as I am aware, it has not as yet found its way into any English text-book of chemistry; but its extreme simplicity and its manageability render it peculiarly suitable for lecture demonstrations, while it has also a special interest as illustrating those *secondary actions* which take place in electrolysis in many cases. The experiment is not original, and I am indebted for it to Prof. Wislicenus of Würzburg, of whose excellent "*Lehrbuch*"† I have made very free use for some years past.

An ordinary three-tubed voltameter of Hoffman's form, such as is commonly used for the electrolysis of water, is so modified in its construction as to have two carbon pencils of the material used in the ordinary Bunsen-cell introduced to serve as electrodes, one at the bottom of each of the two tubes, which are furnished at the top with stop-cocks; the carbon pencils being inserted through corks, which plug the tubes, and are made to carry platinum wires for connection with the conducting wires of the battery.

The actual electrolyte is a concentrated solution of sodium chloride, and with this is mixed about one-tenth of its volume of the strongest solution of ammonia. By the substitution of carbon for platinum the action of the nascent chlorine upon that metal, which would vitiate the results, is obviated.

In a few minutes, with a fairly strong battery (4 to 6 Bunsen or Grove cells), a considerable volume of each of the gases N₂ and H₂ is liberated in the separate tubes, the volume of the latter being three times that of the former, and these are tested in the usual manner.

The following scheme may be taken as accurately representing what goes on:—



The HCl is of course fixed by some of the undecomposed ammonia (6NH₃ + 6HCl = 6NH₄Cl), and, remaining in solution as NH₄Cl, does not interfere with the volumetric results.

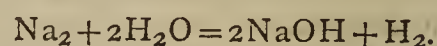
It will be seen that nothing is assumed here but—

(1.) The axiom that things which are equivalent to the same thing are equivalent to one another.

* Mr. Crookes has, however, shown that lime brings out the bands of samarium; but may it not be that the production of other fluorescence opposes the ordinary action of lime?

† "*Lehrbuch der Anorganischen Chemie*," § 147.

(2.) The known reaction of sodium on water,—



(3.) The equally well known reaction of chlorine upon ammonia, 3Cl₂ + 2NH₃ = 6HCl + N₂.

(4.) The law of Avogadro.

Upon these the following train of reasoning is based without much difficulty:—

Starting with the decomposition of the NaCl, and confining our attention at first to what takes place at the negative pole, where Na is removed from the salt and where the free H₂ appears, we know that for every three molecules (or six atoms) of H₂ set free 6H₂O has undergone decomposition; from the known composition of NaCl and known electrolytic laws we know that the removal of 6 atoms of Na at the cathode must be accompanied by the release of 6 atoms of chlorine at the anode; and from the known composition of HCl (the only known compound of these two elements) we know also that these 6 atoms of chlorine must take up 6 atoms of H, the equivalent of the 6 atoms (3H₂) liberated at the cathode; and from these 6 atoms of H in the ammonia, two atoms (1 molecule) of N₂ are set free, as seen in the experiment.

It need scarcely be added that, for the demonstration of the proportion which a given volume of NH₃ bears to the sum of the volumes of the N₂ and H₂ produced by its decomposition, under the same physical conditions, the decomposition of the dry gas by the spark stream in a eudiometer over mercury is as necessary as ever.

Wellington College, Berks.
July 2, 1886.

ON THE DETECTION OF CALCIUM IN THE PRESENCE OF STRONTIUM.

By C. L. BLOXAM.

If a solution of calcium sulphate be mixed with ammonia and a little solution of arsenic acid, it yields, on stirring with a glass rod, a highly crystalline precipitate, which is deposited very strongly on the lines where the glass rod has rubbed the tube. Under an inch objective, this precipitate is seen to consist of fine needles and flat rectangular prisms, and agrees with the description given by Wach of the salt CaNH₄AsO₄·7Aq. This precipitate is nearly as insoluble as calcium oxalate. A solution containing Ca in 113,235 of water, which gave a distinct crystalline precipitate almost immediately with ammonia and ammonium oxalate, also gave one, after a minute or two, with ammonia and arsenic acid, and this precipitate was far more crystalline than the oxalate.

When strontium chloride is precipitated by excess of sulphuric acid, the minute quantity of strontium left in the solution is not precipitated by ammonia in excess and arsenic acid, though it gives a slight precipitate with ammonia and ammonium oxalate.

A solution containing one part (0.0381 grain) of calcium and fifty parts of strontium, acidulated with HCl, precipitated by H₂SO₄, filtered, mixed with excess of ammonia, cooled, and stirred with a little solution of arsenic acid, gave a copious crystalline precipitate. With one part (0.019 grain) of calcium and 100 parts of strontium the precipitate appeared after two or three minutes.

With the same weight of calcium and 500 parts of strontium, the filtrate from the SrSO₄ was evaporated to a small bulk, mixed with excess of ammonia, filtered from a further deposit of SrSO₄, and stirred with arsenic acid; in a few seconds the precipitate of ammonium-calcium arsenate was deposited on the lines of friction, and identified by the microscope.

Samples of strontium nitrate and carbonate, purchased as pure, were found to contain much calcium when examined in this way.

The ammonium-magnesium arsenate appears, under an inch glass, in tufts of minute needles, and could not be mistaken for the calcium salt.

King's College, July 5, 1886.

EYSTER'S SCHEME FOR QUALITATIVE ANALYSIS.

By ROBERT B. WARDER.

IN the *American Chemical Journal* (vol. vii., pp. 21-26) appears a method for the qualitative determination of the bases without direct use of hydrogen sulphide, which will prove very convenient in many cases. Having used this method in part with my own classes during the past year, a few notes may be of service to those who have not yet tried it.

The use of sulphuric acid to precipitate Ba, Sr, Ca, and Pb (as copied from Zettnow's scheme) appears to be a needless complication, and may be simply omitted, other provision being made for the detection of these metals.

The principle underlying Eyster's most important modification will be seen at a glance from the following table, from which also an outline of the scheme may be deduced.

Basis of Usual Scheme.		Basis of Eyster's Scheme.
Sulphides precipitated by H_2S in presence of HCl .	Sol. in Am_2S	<div> <div>As</div> <div>Sb</div> <div>Sn</div> </div> Sulphides sol. in Am_2S .
	Insol. in Am_2S	<div> <div>Hg</div> <div>Pb</div> <div>Bi</div> <div>Cd</div> <div>Cu</div> <div>Ni</div> <div>Co</div> <div>Zn</div> <div>Mn</div> <div>Fe</div> <div>Al</div> <div>Cr</div> </div> Insol. in cold dilute HCl Sulphides (or hydrates) precipitated by $AmOH$ and Am_2S .
Not precipitated by H_2S in presence of HCl .		

Cobalt and nickel hold an exceptional position, their sulphides being practically insoluble in cold dilute chlorhydric acid, and yet not precipitated in presence of that reagent by hydrogen sulphide. Under the new scheme they are dissolved by nitric acid, and held in solution by excess of ammonia with the cadmium and copper. Eyster precipitates the four sulphides (after testing for Cu with ferrocyanide), dissolves the cadmium with sulphuric acid, and tests for nickel with the bead in presence of copper. My own experiments shows that cadmium may also be separated from nickel and cobalt by adding ammonium sulphide in presence of potassium cyanide, and the following provisional scheme is offered:—

Add KCy and Am_2S , yellow precipitate, *cadmium*.
Add $C_2H_4O_2$ to filtrate, black precipitate, *copper*.
Add HCl to filtrate, black precipitate, *nickel*.
Look for Co in solution.

This use of acetic and chlorhydric acids was proposed by Mr. J. Swearingen, and has been partially tested in this laboratory by himself and by Mr. E. G. Eberhardt. Acetic acid precipitates copper at once; a part of the cobalt also separates on standing one or two days.

In a mixture of cobalt and nickel sulphides, the former (as is well known) can usually be detected at once with the borax bead. The latter may be partly dissolved in yellow ammonium sulphide and re-precipitated by chlorhydric acid. I have rarely failed to obtain a sufficient quantity of nickel by this means to give distinct colour to the bead.

Details will be found in Eyster's careful paper, which has induced me to present these notes at once, instead of waiting to make a more thorough examination of the special features proposed.—*American Chemical Journal*.

THE ATOMIC WEIGHT OF SILVER AND PROUT'S HYPOTHESIS.*

By LOTHAR MEYER and K. SEUBERT.

THE calculation of the atomic weights of many of the elements depends, as is well known, upon that of silver, so that the sharpest possible determination of this is desirable in order to obtain accurate results, without which a discussion of Prout's hypothesis, *as far as this is concerned with facts*, is unprofitable.

For this reason J. S. Stas, in his masterly investigations, used the utmost care in fixing the stoichiometrical relations between silver and oxygen, and confirmed these by indirect methods with wonderful accuracy. The hypothesis of Prout, that all atomic weights are rational multiples of that of hydrogen, is not borne out by Stas's work; even when the relation of oxygen to hydrogen = 15.96:1 is rejected as doubtful, and 16:1 is taken in its stead, silver and a number of other elements—among them those whose ratio to hydrogen is most accurately known, differ in their atomic weights far more from whole numbers than experimental errors can account for. The accuracy and reliability of Stas's results seemed so far beyond all doubt that one of the most celebrated advocates of Prout's hypothesis could explain the contradiction of the theory by the experiments only by questioning the stability of the foundation of the atomic theory, *the constancy of chemical proportions*, and consequently the possibility of preparing chemically pure substances.†

In 1878 Dumas,‡ also a supporter of Prout's teaching, published the results of a few experiments, in which he succeeded in separating oxygen from pure silver which had been fused with a mixture of borax and saltpetre. A kilogram. of the silver was heated to redness in a flask connected with a Sprengel's pump, and the evolved oxygen collected and measured.

For each kilogram. of silver there were obtained, in four different experiments, 82, 226, 140, and 249 m.grms. of oxygen.

As Stas subjected the silver used in his investigations to the same treatment, this too, as Dumas claimed, must have contained oxygen. In spite of all the care and skill of the experimenter, his results with metallic silver were affected by a constant error which increased the atomic weight of the silver and lowered those of the halogens; the relation of silver to chlorine, instead of being 108:35.47, as was then generally believed, became 108:35.5, in accordance with Prout's hypothesis.‖

It cannot be denied that this objection is worthy of attention, and we are justified consequently in briefly considering its effect on the result by briefly discussing a few experiments.

If Stas really worked with silver containing oxygen his error will consist in this, that instead of using 1000 parts of silver he used only 999.751 parts.§ In transforming

* See *Berichte der Deutschen Chemischen Gesellschaft*, xviii., 1098 Translated by W. S. Bayley.

† Marignac, *Archiv's des Sciences Physiques et Naturelles* (nouv. per.), ix., 1860, p. 105 and ff. "Il ne m'est pas absolument démontré, que bien des corps composés ne renferment pas constamment et normalement un excès, très-faible sans doute, mais sensible dans des expériences très-déliées, de l'un de leurs éléments." See also *Ann. Chem. Suppl.* 1V., p. 202.

‡ *Comptes Rend.*, lxxxvi., 65—71. *Ann. Chim. Phys.* [5], xiv., 289.

§ A conclusion of Dumas's which can be contested on more grounds than one. See below.

‖ In the most unfavourable case, when the silver contains the largest amount of oxygen observed by Dumas, viz., 0.249 part per 1000.

silver into silver chloride, Stas obtained by four different methods* :—

From 969.3548 grms. Ag 1287.7420 grms. AgCl,
in which Ag : AgCl = 1 : 1.32845.

This relation is changed by Dumas's correction into—

969.1134 grms. Ag = 1287.7420 grms. AgCl,
or Ag : AgCl = 1 : 1.32872.

In the same way the correction may be applied to the cases in which silver was changed into silver bromide or iodide by synthesis. In all these cases the error might possibly have reached the maximum as observed by Dumas.

Fortunately, however, a number of experiments were made from which the amount of oxygen contained in the silver can be determined. These consist of *complete syntheses of silver bromide and silver iodide*, when the amounts of both constituents used as well as the resulting compound were weighed.

In both cases the weight of the product was found to be somewhat too low, a result which can be referred to the oxygen in the silver.†

The complete synthesis of the silver bromide yielded these figures‡ :—

Ag : Br : AgBr = 210.5711 : 156.0098 : 366.5639 grms. [4]
 $\begin{array}{r} \text{Ag} + \text{Br} = 366.5809 \\ \text{AgBr} = 366.5639 \\ \hline \text{Difference} \quad 0.0170 \end{array}$

Calculated for the amount of silver used, this difference corresponds to 0.08073 part of oxygen in 1000 parts of silver, provided the total loss were due to escape of oxygen. The corrected weight of the silver then becomes 210.5541 grms.

Then Ag : AgBr = 210.5541 : 366.5639
 $= 1 : 1.74095$
 Instead of $1 : 1.74081$.

Similarly, in the complete synthesis of silver iodide, the weight of the product is less than the sum of the weights of iodine and silver.

Stas found§ :—

Ag : I : AgI = 324.2571 : 381.1262 : 705.3718 grms. [5]
 $\begin{array}{r} \text{Ag} + \text{I} = 705.3833 \\ \text{AgI} = 705.3718 \\ \hline \text{Difference} \quad 0.0115 \end{array}$

This difference corresponds to 0.03547 parts of oxygen in 1000 of silver, so that the weight of pure silver used was 324.2456 grms. Consequently—

Ag : AgI = 324.2456 : 705.3718
 $= 1 : 2.17542$
 Instead of $= 1 : 2.17535$.

The comparison of these values with those obtained from the analyses of the chlorates, bromates, and iodates gives the relation of silver to oxygen.

Stas found—

AgClO₃ : AgCl = 398.3177 : 298.4250 grms. || [2]
 AgBrO₃ : AgBr = 188.5332 : 150.1671 grms. ¶ [2]
 AgIO₃ : AgI = 331.6101 : 275.3235 grms. ** [3]
 Or, AgCl : O = 8.9614 : 1
 AgBr : O = 11.7420 : 1
 AgI : O = 14.6742 : 1.

* Lothar Meyer and Karl Seubert, *Die Atomgewichte der Elemente*. Leipzig, 1883, pp. 55 and 56, No. 41 g.

† As the difference in the case of the synthesis of silver bromide was smaller the more carefully the bromine was dried, this must in part be due to moisture in the bromine. Besides there was a small loss occasioned by washing.

‡ *Die Atomgewichte der Elemente*, &c., p. 57, No. 42 b, β.

§ *Ibid.*, p. 59, No. 43 b, γ.

¶ *Ibid.*, p. 47, No. 35 b.

¶ *Ibid.*, p. 47, No. 36.

** *Ibid.*, p. 41, No. 37 b.

Evidently these figures cannot be influenced by Dumas' correction, as there was no metallic silver weighed. From these figures the relation of the silver to the oxygen can easily be calculated by means of the formula*—

$$\frac{\text{Ag}}{\text{AgR}} \cdot \frac{\text{AgR}}{\text{O}} = \frac{\text{Ag}}{\text{O}},$$

in which R is one of the halogens Cl, Br, or I. According to this,—

$$\text{Ag} : \text{O} = \frac{8.9614}{1.32872} = 6.7439 : 1$$

$$\text{Ag} : \text{O} = \frac{11.742}{1.74095} = 6.7446 : 1$$

$$\text{Ag} : \text{O} = \frac{14.6742}{2.17542} = 6.7455 : 1.$$

Of these three numbers, neither of which agrees with the 6.7500 demanded by Prout's hypothesis, the third is entitled to most consideration; for, in the first an arbitrary correction is made, in the second a part of the error credited to oxygen must surely be due to some other impurity, the third is calculated from experiments made with the purest materials. This number, 6.7455, obtained from the complete synthesis of silver iodide and the analysis of the iodate, is also the mean of several other determinations made by Stas which vary between 6.7451 and 6.7458; besides, it is almost identical with 6.7456 yielded by silver iodide and iodate without the application of Dumas's correction, as well as the 6.7456 obtained by reducing silver sulphide and sulphate.

The conclusion is consequently justified, since several of Stas's determinations agree satisfactorily with one another and with the number which is certainly free from the error pointed out by Dumas, that the influence of this is confined within the limits of error, and consequently may be neglected.

If it appears strange that the silver used by Stas for determining the atomic weight exhibited only in small degree an impurity, whose amount was determined by the experiments of Dumas as being quite considerable, it must be remembered that only the oxygen present in a condensed form would influence the weight; the gaseous oxygen under the normal pressure producing an effect scarcely more noticeable than the air in which the silver was weighed. Besides, Stas always heated his silver to dark redness immediately before weighing, so that the greater part of the "occluded" oxygen either escaped or was changed into the gaseous form.

These considerations, based on the results of experiments, show, as we again emphasize, that the determinations of the atomic weight of silver by Stas are not appreciably influenced by the oxygen which the silver retains within itself.†

The atomic weight of silver then is, if H = 1 and O = 15.96,—

$$\begin{array}{l} \text{Ag} = 107.66 \\ \text{if } \text{O} = 16, \text{Ag} = 107.93; \end{array}$$

while the figures calculated from the results of the experiments with metallic silver and silver chloride are, after applying the correction of Dumas,—

$$\begin{array}{l} \text{Ag} = 107.63, \text{ if } \text{O} = 15.96, \text{ and} \\ \text{Ag} = 107.90, \text{ if } \text{O} = 16.00 \end{array}$$

Thus we see that the atomic weight of silver is removed still farther from the whole number required by Prout's hypothesis, by the application of Dumas's correction; chlorine also still remains inconsistent with it, while a few other elements, like potassium, sodium, &c., approach or depart from it according as we take O = 16 or 15.96. Dumas has assumed, in order to explain such exceptions to Prout's hypothesis as chlorine particularly offers, that

* *Die Atomgewichte der Elemente*, &c., pp. 50—52.

† W. Ostwald reached the same conclusion through the theory of probabilities. See his "Lehrbuch der allgemeinen Chemie," 1884, i., 35.

hydrogen itself is composed of ultimate atoms (uratomen), of which he at first thinks there are two in one atom of hydrogen, but when this is also found not to be in accordance with the experimental results, increases the number to four.

But even this "elastic modification," as Clarke calls it, of the old theory can only be preserved, in the face of Stas's work, by decreasing the size of the unit, that is the weight of the ultimate atom, in proportion as the accuracy of our experimental work increases.

More recently,* the universal ether, with an atomic weight of 0.0001 ($H=1$), has been assumed as the primitive substance of which all other elements were formed. The atomic weights of all other elements must of course be whole multiples of this, since none of them have been accurately determined to the fourth decimal place, while many are certain only to the first or second place, and some only to units of hydrogen.

Nor need it excite wonder if, as has been proposed by another writer,† every atomic weight y can be approximately calculated by the expression:—

$$y = p \cdot 15 - 15 (0.9375)^x \text{ or,} \\ y = 15 \left(p - \left(\frac{15}{16} \right)^x \right),$$

in which p may vary between 1 and 16, but x varies from 1.50, or even ∞ ; for the fraction $\frac{15}{16}$ so nearly approaches unity that any number can be accurately expressed by the formula.

Speculations of this kind are far removed from any possibility of experimental proof, and can therefore never be expected to receive from it any support. Nor can we ever hope to receive any essential extension of our knowledge in respect to primitive matter (urmaterie) through a more accurate establishment of the atomic weights; the next important progress will rather be brought about by the decomposition of the elements into a similar substance, differing from them, however, which may be the primitive matter itself, or a condensation product of it. The solution of this question, that is, the decomposition of all the elements into one and the same original substance, we can hardly ever expect to accomplish.

From the atomic weight of silver, determined, as above shown, with the greatest accuracy, and from those of the other important elements‡ calculated by its means, it follows as a consequence that *the atomic weight of silver, as well as the atomic weights of numerous other elements, all contradict Prout's hypothesis in its characteristic original conception; it must, therefore, be looked upon as having been disproved by experiment.* In its new forms it has likewise been disproven, so far as this is possible in the present state of our knowledge. Beyond this it amounts merely to philosophical speculation concerning an idea whose probable correctness will be denied by no one,§—the unity of matter.

THE ABSORPTION-SPECTRA OF OXYGEN.

By J. JANSEN.

THE spectral study of oxygen has led the author to detect in this gas several orders of absorption phenomena. At the first is the elective action, which is manifested by the system of fine rays, first recognised by M. Egoroff. According to this author they are especially the groups A,

B, and α . But besides—and here the phenomena become deeply interesting—there exists another system, consisting not of lines easily individualised, but of bands which appear very difficult to resolve. This system appears much later than the foregoing, but it is rapidly developed with the increase of density, and soon acquires the upper hand.

The two systems differ so widely in the conditions of their production that the first may be obtained without the second, and *vice versa*. But the point of chief importance for molecular mechanics, and, as will soon be seen, for celestial physics, is the law according to which these absorption phenomena are developed when the density and the thickness of the medium traversed by the luminous pencil are made to vary simultaneously. It then appears that the bands are developed much more rapidly than according to the product of these two factors. To represent the phenomena the thickness traversed must be multiplied not by the density of the medium, but by its square.

Thus these bands have been obtained in a tube 0.42 metre in length, filled with oxygen at the pressure of 70 atmospheres only, whilst calculation would show nearly 860 atmospheres if—setting out from the experiment with a tube of 60 metres—we wished to fulfil the law of the product of the length by the density, *i. e.*, the condition of causing the pencil to traverse the same quantity of matter by weight.

The bands in question are the same as those mentioned in a former communication. The author then asked why these bands, obtained with thicknesses of oxygen much less than those which the light of the sun is obliged to traverse before reaching us, are not very distinctly shown in the solar spectrum? We have now the explanation of this fact, which follows from the law of the variation of these actions according to the density of the medium in which they are produced, as it will be shown. Such are the general outlines of the phenomenon in question. We shall next have to enter into the details of its exact description and applications, as well as the investigation of analogous phenomena in other gases.

In his next communication the author will describe the series of experiments which have served to demonstrate that the phenomenon in question belongs to oxygen gas. —*Comptes Rendus*, vol. cii., p. 1352.

NOTES FROM THE LABORATORY OF THE CHEMICAL EXAMINER TO GOVERNMENT, BURMA.

By R. ROMANIS.

Agricultural Experiments.

TEN plots were manured with ground bones, dissolved bones, and nitre for three years. The result shows that ground bones are the most economical manure for rice in the soil of the Irrawadi delta. The largest crop was given by a mixture of 10 cwts. ground bones with 1½ cwts. nitre per acre, viz., 2890 lbs. of grain against 1940 lbs. by the unmanured.

Composition of Grain Grown with Various Manures.

	I.	II.	III.
	2 years unmanured.	1st year, Ground Bones. 2nd year, No manure.	Bones, 2 years.
Cellulose	10.78	10.10	8.94
Alkaline extract ..	13.20	12.30	10.43
Alcoholic extract ..	2.24	1.20	1.93
Water extract	2.35	2.87	2.23
Benzol extract	4.93	2.18	3.31
Starch	66.72	70.60	73.13

* M. Zängerle, "Über die Natur der Elemente, &c." "Program des Kgl. Realgym. München," 1882.

† Edm. J. Mills, "On the Numerics of the Elements," *Phil. Mag.*, Nov. 1884, p. 393.

‡ Cf. Atomic weight tables of Meyer and Seubert. "Breitkopf u. Härtel," Leipzig, 1884.

§ Cf. Lothar Meyer, "Moderne Theorien," V. Auf., p. 134.

Ash of Rice. (By J. TSAW OS WHITE.)

	Unhusked.	Husked.
Potash	7.35	16.99
Soda	0.53	2.03
Lime	0.66	1.19
Magnesia	3.03	11.76
Ferric oxide	2.46	2.38
Phosphoric acid	10.65	45.96
Silicic	75.32	19.69

Ash of Indigo Stem.

Potash	42.22
Soda	5.97
Lime	18.54
Magnesia	6.27
Ferric oxide	1.06
Phosphoric acid	12.55
Sulphuric	8.45
Silicic	4.92

Ash of Juice of Sugar-Cane Grown at Two Different Localities.

	I.	II.
Potash	33.80	36.09
Soda	19.40	2.25
Magnesia	1.42	7.81
Lime	1.38	1.39
Ferric oxide	1.59	2.17
Phosphoric acid	3.92	11.32
Sulphuric	35.33	23.24
Silicic	3.33	9.46
Chloride of potassium	—	6.24
	100	100

No. I. came from a district near the sea; the sugar is said not to crystallise. No. II. is the same cane grown at Rangoon; it crystallised without difficulty.

Specimen of Jade from Mogaung, found in the Palace at Mandalay. (By J. T. OS WHITE.)

Silica	49.13
Alumina	19.26
Ferrous oxide	6.56
Lime	11.33
Magnesia	5.80
Potash	0.91
Soda	7.07
	100.06

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

June 26th, 1886.

Prof. W. E. AYRTON, F.R.S., Vice-President, in the Chair.

MR. E. M. LANGLEY was elected a member of the Society.

The following communications were read:—

"On certain Sources of Error in connection with Experiments on Torsional Vibrations." By HERBERT TOMLINSON.

During a long series of researches on the torsional elasticity and internal friction of metals the author has come across the following sources of error in connection with torsional vibrations. In some of the earlier experiments a horizontal brass bar was suspended by a wire and oscillated, the times of oscillation being observed by the ordinary lamp, mirror, and scale. The moment of

inertia was varied by sliding two brass cylinders suspended from the bar by fine wires backwards and forwards along it. It was then found that, under certain conditions, the bar executed a few vibrations of rapidly decreasing amplitude, came to rest, and then commenced to swing again, the amplitude increasing to a maximum, again decreasing, and so on. This effect was finally traced to an approach to synchronism between the time of oscillation of the bar and that of the small cylinders about their axes of suspension, the absorption of energy being due to these being set in vibration. The effect entirely disappeared upon clamping the cylinders rigidly to the bar. On another occasion, however, the old phenomenon reappeared and, after much time spent in investigating it, was found to be due to a somewhat similar cause, a near approach to synchronism between the periods of torsional and pendulous vibrations. If the axis of the wire passed accurately through the centre of the mass of the vibrator this would not occur; but this condition it is practically impossible to fulfil. Another source of error lies in the fact that in a wire recently suspended the torsional vibration period will always be found to be slightly greater than when it has been suspended for some time and frequently oscillated.

"On a Mode of Driving Electric Tuning-Forks." By Prof. S. P. THOMPSON.

It is invariably found that the frequency of an electrically maintained fork is continually changing. This great inconvenience the author believes to be due to the fact that the impulses are given to the prongs at a disadvantageous moment, namely, when they are at the extremities of their swings. It is desirable that the impulse should be given at the middle of the swing, and to effect this it is suggested that each fork should make and break the circuit of the magnet influencing the other one, and it was shown how the electrical connections could be made to effect this in a simple manner.

"A Further Note on the Formula of the Electro magnet and of the Dynamo." By Prof. S. P. THOMPSON.

In a paper recently communicated by the author it was shown that an expression given by Fröhlich for the intensity of magnetisation in terms of the magnetising force was nearly identical with one derivable from a simple law enunciated by Lamont. In a recent paper Fröhlich has further developed this law, and in the present paper the author has extended Fröhlich's results, and has applied them to the various forms of dynamos.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, July 5th, 1885.

WILLIAM HUGGINS, D.C.L., F.R.S.,
Vice-President, in the Chair.

THE following were elected Members:—Mr. George A. Crawley, The Right Hon. W. H. Smith, M.P.

The Managers reported that they had re-appointed Professor James Dewar, F.R.S., as Fullerian Professor of Chemistry.

The Presents received since the last Meeting were laid on the table and the thanks of the Members returned for the same.

Patent Office Library.—We are requested to state that the Free Public Library at the Patent Office, 25, Southampton Buildings, Chancery Lane, W.C., will, on and after July 1st, 1886, be open to the public daily from 10 a.m. to 10 p.m., instead of, as heretofore, from 10 a.m. to 4 p.m. This library, in addition to the Specifications, Indexes, and other publications of the Patent Office, contains a large collection of the leading British and Foreign Scientific Journals, Transactions of Learned Societies, and Text-books in the various departments of Science and Art.

NOTICES OF BOOKS.

Frictional Electricity. By T. P. TREGLOHAN, Head Master of St. James's Science and Art Schools, Keyham, Devonport. London: Longmans and Co.

ALMOST at the very outset of his work the author makes the judicious remark that "It should be the object of everyone studying this subject (and of course the same rule applies to every department of physical science) to test every phase of it by as many experiments as possible, that the mind may be familiarised with the simple phenomena which have led to marvellous discoveries." This dictum he enforces by quotations from Profs. Tyndall and Guthrie. The former of these authorities shows the necessity for learning the art of experimentation, and tells us, most truly, that thought springing from this source has "a vitality not derivable from mere book knowledge." Prof. Guthrie, in his annual report on the "Examination of Training Colleges" (1882) complains that "In many cases the teaching appears to have been mainly theoretical. Many of the answers show that the examiner [? examinee], while understanding the conventional description of a piece of apparatus, has probably never seen it, and certainly never used it. This won't do."

It is surprising how anyone can fail to see how, from these two quotations alone, must follow the condemnation of the entire English system of education as far as the physical and natural sciences are concerned. For if the arts of observation and experiment, and of drawing correct inferences from the phenomena encountered, constitute the true object of the student, what ensues? His proficiency in these arts, his suggestiveness, his intellectual resources can never be judged by an examiner, much less appraised in "marks." Hence, where the gaining marks is the goal aimed at, the student will be judged chiefly by his power of remembering other men's discoveries, and of talking about things rather than doing them.

In a work which makes such admissions as those we have just quoted, it strikes us as an incongruity when we are told that "the present volume has been prepared to meet the syllabus of the Science and Art Department for the Elementary Stage, and to satisfy the requirements of the second stage of one of the Physics Courses of the 'Mundella Code' as laid down by the Education Department."

As an Appendix we find the questions given out in frictional electricity by the Science and Art Department from 1867 to 1885 inclusive.

There is here one plain question which we feel compelled to put to all upholders of the examinational system of education: How is it that Germany not only produces a much greater quantity of valuable scientific research than does Britain, but that Germans are more and more supplanting natives in our laboratories, museums, &c. Either we as a race are intellectually inferior—an alternative which we cannot admit if we remember Newton, Young, Davy, Faraday, Graham, Darwin, Balfour, Lyell, and many others—or we are moving in the wrong direction as regards higher education.

The subject-matter of the book before us is, as it might be expected, free from errors, and its arrangement is very satisfactory.

Analytical Chemistry: a Series of Laboratory Exercises constituting an Elementary Course of Qualitative Chemical Analysis, Compiled for the Use of Beginners in the Laboratory. By W. DITTMAR, F.R.S., F.R.S.E., Professor of Chemistry in Anderson's College, Glasgow. New Edition. London and Edinburgh: W. and R. Chambers.

THE first edition of this little work appeared in 1879. It had been in use in the laboratory of Anderson's College

for above a year previous to its publication, and, as the author assures us, has been of great service to students.

The second edition, now before us, contains in its first part little addition or alteration, save as regards the section on Bunsen's flame-tests (p. 13), which has been contributed by Dr. Gibbs, of the Edinburgh University.

The Appendix, or purely medical portion of the treatise, has been entirely re-written.

We notice with pleasure that the work contains no reference to any "syllabus" or examination, the author's evident object being to train up his students not to "pass," but to "know,"—a very different matter.

The Camera. A Monthly Magazine for those who practise Photography. Vol. i., No. 1. June 1, 1886.

THE increase in the number of scientific journals is, we fear, out of proportion to any improvement in the demand.

Our young contemporary begins with a paper on "Photography and Astronomy," which expounds one portion—and only one—of the important services which photography is now rendering to the sciences.

Mr. J. S. Hodson, in an able article entitled "Photography in its Relation to Artistic Reproduction," seems—like too many persons in the present day—unable or unwilling to recognise the boundary between Science and Art.

We note a curious paragraph, which seems to question the instantaneous character of the illumination afforded by a lightning-flash. Mr. A. S. Barber, of Philadelphia, "claims to have made two negatives of lightning subjects at night-time, the only illumination being from a single lightning-flash. Both pictures exhibit foliage which has moved during exposure. The *Journal of the Franklin Institute*, which publishes this strange information, will not vouch for the accuracy of the deductions made. We are inclined to follow the same course,"—a very prudent reservation.

La Vara de Esculapio. Vol. i., Nos. 1 and 2.

THIS new hygienic journal, which appears fortnightly at Barcelona, bears the motto "Hominum sanitas suprema lex esto," and may be regarded as a movement in the right direction. It seems to wage war especially against quackery and adulteration. As a specimen of the former evil it mentions the "neurate of gold," a proprietary medicine lately introduced into Spain, and which is said by the makers to consist of "nerve-molecules, combined with gold." It is edifying to see how skilfully the charlatans of the present day catch up and utilise scientific terminology.

As regards adulteration the state of Spain must be unsatisfactory. We find that the editors, having visited a great number of wine and vinegar shops, have not met with pure wine or vinegar in any of them. We wish our contemporary success. He will evidently find a superabundance of work.

Industries. A Journal of Engineering, Electricity, and Chemistry for the Mechanical and Manufacturing Trades. Vol. i., No. 1.

THE bulk of this new technical paper is devoted to subjects which do not fall within our cognisance. Thus we find here articles on diamond-mining and diamond-cutting, on Admiralty and dockyard administration, on cask-making machinery, on coal-getting machinery, Japanese industries, the "Manchester Guardian" office, the mining prospects of South Staffordshire, &c. There is a relatively brief department of industrial chemistry conducted by Mr. Watson Smith, of the Victoria University.

Perhaps the most satisfactory feature, from our point

of view, is the article on technical education taken in conjunction with passages in other parts of the journal bearing on the same momentous question. It is here admitted that "until our educational arrangements are improved we must expect to see large numbers of Germans employed in our drawing offices and engineering establishments—we may add "in our laboratories and chemical works." But are our educational arrangements in process of improvement? Do not our movements in this sphere consist mainly in multiplying examinations? In the journal before us we read elsewhere "in Britain, at present, in the excitement about technical education, a great deal of what passes under that name does not deserve to be called *education*; it is mere cramming the facts, figures, and methods of work, which may be useful enough in the way of instruction when superadded to education, but by itself is not only useless, but very likely may become worse than useless in engendering a condition of mind in the students which unfits them for original thought."

Industries has before it a field in which there is scope for good work.

Patent Centrifugal Drying, Separating, and Filtering Machines.

MESSRS. WATSON, LAIDLAW, AND Co. have forwarded us a catalogue of improved devices and appliances which must be found of no small importance to dyers, chemical manufacturers, &c. The firm have produced small centrifugals, of 18, 12, and even 8 inches diameter, suitable for experiments on the small scale, and even for laboratory purposes. These machines may be driven by hand, but they can also be arranged to be propelled by electric power at 2000 to 4000 per minute. We should recommend this catalogue to the attention of our readers.

CORRESPONDENCE.

PURIFICATION OF AIR.

To the Editor of the Chemical News.

SIR,—In two letters in your valuable Journal—the one on June 18th from Mr. R. Warrington, F.R.S., and the other on June 25th from Dr. Percy Frankland—reference is made to a paper communicated to the Royal Society by the latter gentleman on June 10th, to the effect "that air when passed slowly through a 2-foot tube, coated internally with gelatin, deposits practically the whole of the micro-organisms which it carries in suspension, within the first half of its course through the tube."

This fact is not new, but was, I believe, first noticed by Hesse, and by him (*Mittheilungen aus dem K. Gesundheitsamte*, Band iii., p. 182), was made the basis of a very convenient and elegant process for the determination of the number of micro-organisms in air.

This method I have used, in conjunction with Drs. Haldane and Anderson, in an extensive investigation of the Air of Dwellings and Schools, more particularly in reference to Disease. The results of this research we communicated to the Royal Society, through Sir Henry Roscoe, on the same day (June 10th) as Dr. Percy Frankland's paper.

The same method we also recently adopted in an examination of the air in the sewers under the Houses of Parliament, an investigation which we undertook at the request of the Select Committee on the Ventilation of the House; also in a series of experiments with which we are at present engaged on the air in the sewers of Dundee. One of the chief results of our investigation of the air of sewers is that they behave practically like

Hesse's tubes, so that sewer air contains, as a rule, fewer micro-organisms than the outside air at the same time.

The further interesting fact appears also to have been noticed by Dr. P. Frankland, that, though the air in its passage through the tube has deposited all its micro-organisms, it may still contain an abundance of suspended matter. We have also observed this phenomenon in our researches, and referred to it at length in our paper to the Royal Society. We have suggested a method by which the number and relative density of the dust particles in air may be determined, at the same time as the micro-organisms. The paper was also accompanied by a photograph illustrating the phenomenon in question. I quite agree with Dr. P. Frankland that the deposition of the micro-organisms and dust in passing through a tube is due to gravity alone, for like him, and as Hesse also observed, we have always found that they are practically confined to the *bottom* of the tube.

In this connection it is also interesting to note that moulds, as a rule, settle out much less rapidly than bacteria; a fact which, I think, was first observed by Hesse.—I am, &c.,

THOS. CARNELLEY.

University College, Dundee, June 30, 1886.

"ALLOTROPIC NITROGEN."

To the Editor of the Chemical News.

SIR,—In a "Note as to the Existence of an Allotropic Modification of Nitrogen," communicated by Miss K. J. Williams and Professor Ramsay to the Chemical Society, June 17th, 1886, and reported in your last issue, the authors describe experiments which they describe as "testing my statements" as to the existence of an allotropic modification of nitrogen.

Their results, which they say "fail to corroborate" mine, are briefly as follows:—

7.7 litres of nitrogen gas, obtained from a mixture of potassium nitrite and ammonium chloride in aqueous solution by the application of heat, and of crystals of cupric chloride, yielded ammonia, corresponding to 0.00005 gramme of nitrogen. *Qualitatively*, these results do corroborate mine, since ammonia was obtained from the purified nitrogen, mixed with hydrogen and passed over platinum sponge.

I presume, therefore, that the failure to corroborate alluded to by the authors had reference to the *quantity* of ammonia produced.

The only *quantitative* estimations of the yield of ammonia obtained from a given volume of nitrogen gas published by me are to be found in my book, "On Certain Indications of the Existence of an Allotropic Modification of Elementary Nitrogen, and on the Synthesis of Ammonia," (J. and A. Churchill, 1885). For reasons fully detailed in that work (pp. 18 to 20), I discarded the use of a mixture of ammonium chloride and potassium nitrite altogether in making *quantitative* estimation of the proportion of active nitrogen in the gas obtained by heating solutions of ammonium nitrite, and employed for that purpose a pure solution, prepared by passing N_2O_3 (or the yellow gas resulting from the action of HNO_3 upon As_2O_3) into a solution of ammonia of sp. gr. 0.880 (*vide pp. 21 et seq.*).

My results tended to show that as much as 1 per cent of the gas was active.

Therefore, as regards the *quantity* of ammonia produced, my results are enormously discrepant from those of Miss Williams and Prof. Ramsay; but, as the conditions of our respective experiments also differed widely, I do not think that any importance can be attached to the comparison.—I am, &c.,

G. STILLINGFLEET JOHNSON.

King's College, London, July 5, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cii., No. 25, June 21, 1886.

Certain Double Phosphates of Thorium and Potassium and of Zirconium and Potassium.—L. Troost and Ouvrard.—The composition, crystalline form, and the properties of thorium metaphosphate have shown that no argument can be drawn from this salt to assimilate thorium and zirconium and to ascribe to the former the formula of a dioxide rather than of a monoxide. The authors have sought by preparing a certain number of thorium phosphates and analogous compounds of zirconium if it is possible in the dry way to verify the analogy between thoria and zirconia pointed out by different observers. Potassium metaphosphate and pyrophosphate yield, with thorium and zirconium, double phosphates which have analogous compositions, but which are not isomorphous. Potassium orthophosphate yields double phosphates which have different compositions. There is no isomorphism between thoria and zirconia, as obtained by the calcination of the double phosphates at a very high temperature.

Ammonia in Soils.—MM. Berthelot and André.—A voluminous continuation of the controversy with M. Schlœsing, which the authors finish by saying that they have nothing either to add or to withdraw.

Announcement of the Discovery of a New Metal, Austrium.—Lecoq de Boisbaudran.—In the *Monatshefte für Chemie* of April, 1886, appears the announcement of the discovery of a new metal, which the author, Herr E. Linnemann, has named "austrium." According to the description of its chemical properties, the method of its extraction from the orthite of Arendal and its electric spectrum, austrium appears to the author to be very probably gallium, the presence of a small quantity of which in orthite is not surprising. The two rays of austrium, measured approximately by Herr Linnemann, are $\lambda = 403.0$ and 416.5 , those of gallium being 403.2 and 417.05 (the mean of the author's measurements and those of MM. Delachanal and Mermet). In austrium, as in gallium, the ray 417 is the stronger.

Vapours Emitted by a Mixture of Volatile Substances.—P. Duhem.—The author concludes that the equations of equilibrium given by thermo-dynamics render it possible to demonstrate that—"The partial pressure of the vapour emitted by each of the two liquids mixed is inferior to the saturated vapour-tension of the same liquid taken in a state of purity.

Dynamics of the Molecule of Water, Speed of Propagation of Sound; Compressibility, Fusion-Heat of Ice; Specific Heat.—M. Langlois.—A mathematical paper, not susceptible of useful abstraction.

Calorimetrical Study of Iron at Elevated Temperatures.—M. Pionchon.—About 700° iron undergoes a modification characterised by an absorption of heat which is extremely rapid within an inconsiderable range of temperature. In the discussion on reading this paper E. Becquerel remarked that iron, about 600° , presents another very remarkable change in its physical properties, since the attractive action exerted upon it by magnets is then suddenly diminished. As nickel and cobalt, from a magnetic point of view, present effects of the same order, but at different temperatures, nickel at 400° and cobalt at white redness, it would be very interesting to ascertain if the thermic capacity of these metals does not undergo changes analogous to those of iron near those temperatures.

Conditions realising the Maximum of Useful Work in an Electric Distribution.—M. Vaschy.—Not capable of useful abridgment.

Presence of a New Element in Samarskite.—W. Crookes.

Dissociation of Hydrated Copper Sulphates.—H. Lescœur.—The author's conclusions are that the crystalline hydrate has great difficulty in parting with the water which it contains, and also in re-absorbing it, a phenomenon which seems in connection with the hardness of the crystals. If finely pulverised the salt is dissociated more readily, a property which seems connected with the greater surface exposed. If placed in the stove or on a hot plate the product is dehydrated in a most irregular manner, constituting a mixture far from homogeneous, a property which seems to depend on its bad conductivity for heat.

On the Alkaline-Earthy Selenides.—Ch. Fabre.—A thermo-chemical examination of the calcium, strontium, and barium selenides.

Action of Acids and Bases upon Solutions of Tartar-Emetic.—M. Guntz.—The author shows that on adding an acid to such solutions the whole of the antimony is not precipitated, and that the precipitate is not the terhydrated oxide. Bases, on the other hand, precipitate pure anhydrous antimony oxide.

Action of Water and Ammonia upon Methylene Chloride.—G. André.—The destruction of methylene chloride by an aqueous solution of ammonia takes place at a lower temperature than in contact with water alone.

New Properties of Cyanised Camphor.—A. Haller.—The author has obtained campho-carbonic ether, showing that cyanised camphor may be considered as the nitrile corresponding to campho-carbonic acid.

Contribution to the Study of the Alkaloids.—Oechsner de Coninck.—The author has treated with potassa certain pyridic ammonium iodides, obtaining colouring-matters. Pyridin iodomethylate, dissolved in a slight excess of absolute alcohol and treated with potassa takes a fine red colour; excess of alkali turns it to a brownish red and then to a dirty red. The liquid deposits a brown resin which dissolves in alcohol with a deep red colour; hydrochloric acid turns this solution to a bright red, acetic acid to an orange-red, ammonia to a ruby-red, or, in excess, to a dirty red. An excess of water slightly acidified with hydrochloric acid turns it to an orange-red. Pyridin iodoethylate and α -picoline iodomethylate and iodoethylate also give rise to coloured reactions.

On the Normal Dinitriles, $CN-(CH_2)_n-CN$.—L. Henry.—The accumulation of nitrilic nitrogen in the carbonated molecules has a powerful influence upon the properties of the entire molecule, increasing its volatility and rendering it more apt to crystallise.

Chemical Studies on the Products of the Eruption of Etna in May and June, 1886.—L. Ricciardi.—The sands collected and the lavas contain silica, chlorine, phosphoric acid, alumina, ferric and ferrous oxides, manganese, chrome, calcium, magnesium, potassium, and sodium.

Volumetric Determination of Sulphur in Sulphides Decomposable by Hydrochloric or Sulphuric Acids.—Fr. Weil.—A weighed quantity of the sulphide or the ore in question is placed in a small flask fitted with a perforated stopper and a glass delivery tube. This tube plunges into a vessel containing an excess of a normal solution of copper, exactly measured, which is then mixed with an excess of ammonia until it becomes quite limpid and of a fine blue. An excess of hydrochloric acid is then rapidly poured into the flask containing the sulphide, which is placed in communication with the ammoniacal solution of copper. The sulphuretted hydrogen evolved is entirely precipitated as copper sulphide. The flask is heated until the vapours no longer occasion a precipitate

on entering the copper solution. The solution which remains blue from the excess of copper used is either separated from the precipitate by filtration or poured with it into a graduated jar, where it is made up to a given volume by adding the water used in washing the vessel. It is let settle and the copper is estimated in 10 or 20 c.c. of the clear blue solution. For this purpose the 10 or 20 c.c. are introduced by means of a pipette into a colourless glass flask and mixed with about 50 c.c. pure hydrochloric acid. It is heated to a boil and solution of stannous chloride (standardised with pure copper) is added by means of a burette until the liquid is completely decolourised. The volume of stannous chloride employed indicates the quantity of copper in the 10 or 20 c.c. taken, and consequently remaining in the entire volume of the blue liquid after part of the copper has been precipitated by the sulphuretted hydrogen. The difference between the quantity of copper thus found by titration and that originally contained in the volume of the normal copper solution employed gives the quantity of copper precipitated by the sulphur of the sulphides analysed. The quantity of sulphur contained in the portion of sulphide taken can be found by multiplying this difference by the coefficient 0.50393. It is useful to introduce a little granulated zinc into the flask containing the sulphide under analysis.

Researches on the Development of the Sugar-Beet.—Aimé Girard.—Not adapted for abstraction.

Revue Universelle des Mines, de la Metallurgie, &c.,
Vol. xix., No. 2, March and April, 1886.

Experiments on the Ignition of Coal-dust and Fire-damp.—C. Hilt.—The author concludes that the degree of tenuity of coal-dust plays a great part, but the result depends principally on the chemical composition of the coal. Coals containing from 16 to 24 per cent of volatile matter seem more dangerous than either poorer or richer qualities. The ignition is propagated between two distinct spaces, each containing either coal-dust or explosive gaseous mixtures, not only when they are placed in communication by a train of dust, but even when they are separated by a considerable distance free from fire-damp or coal-dust. The ignition of dust may be induced by an explosion of fire-damp as well as by a blast, and the explosion may be occasioned on firing a blast by electricity, as well as by a safety-match or a port-fire. With dynamite there is less danger, and with gun-cotton dissolved in nitro-glycerin practically none, if it is ignited by means of a cap of sufficient force.

Zeitschrift für Analytische Chemie.
Vol. xxv., Part 2, 1886.

Determination of Nitrogen in Wine, Must, and Lees.—Dr. P. Kulisch.—The author recommends Kjeldahl's process as satisfactory.

Determination of Nitrogen by Kjeldahl's Method.—Dr. A. Kindell and F. Hannin.—The authors discuss the error occasioned by the mechanical projection of soda into the acid. They tried the safety tube filled with glass beads, as proposed by Pfeiffer and Lehmann. They found that the beads became very wet from the condensation of water, which spirted again on drying. A deeper stratum of beads was not found to be an improvement. They therefore kept the beads relatively dry by placing the tube containing them within a wider tube traversed by the steam. It was found that a stratum of beads 8 centimetres in height gave, when thus arranged, the required safety. The outer tube is 25 m.m. in diameter; the bead-tube is 10 to 12 m.m., and it is closed below by means of a cap of nickel wire gauze.

An Analysis of Gooseberry Wine.—Dr. L. Marquardt.—The proportion of potassa in gooseberry wine is about

equal to that in grape wines. That of phosphoric acid is relatively smaller. Tartar is found by no means in trifling amounts, equal, in fact, to those found in many grape wines.

New Agent for Thickening Mineral Lubricating Oils.—Dr. L. Marquardt.

Determination of Phenol in Crude Carbolic Acid.—Julius Tóth.—This paper will be inserted in full.

New Method for the Quantitative Determination of Uric Acid.—J. B. Haycroft.—Apparently from an English source.

Behaviour of Plumbiferous Zinc on Re-melting.—K. Kraut.—The behaviour of plumbiferous zinc on melting renders it impossible to ascertain the mean proportion of lead in a large number of zinc plates by taking portions for analysis. No matter from how many plates borings or chippings are taken the result of the analyses will never authorise a conclusion as to the quantity of lead in the remaining plates.

Direct Determination of Chlorine in presence of Bromine.—Dr. G. Vortmann.—This paper will be inserted at some length.

Determination of Alumina by Titration.—Dr. K. J. Bayer.—The author refers to his former paper (vol. xxiv., p. 542). He states that the solutions must be very dilute, containing at most 0.1 alumina in 100 c.c. In titrating the reaction of the liquid is kept alkaline to near the end, keeping up a violent ebullition, and at last effecting the change of colour by means of a drop or two of normal sulphuric acid. The author now uses phenolphthalein as indicator in place of litmus. Attempts to precipitate alumina from its alkaline solutions by means of carbonic acid and then titrating the alkali remaining in solution, yielded, for the most part, unsatisfactory results, as the alumina on separation carries down with it much sodium carbonate, forming a peculiar double compound. If, however, a slow current of carbonic acid is passed into a dilute briskly boiling solution, keeping the flask in constant motion, aluminium hydroxide can be obtained free from soda, and the latter can be titrated in the ordinary manner. In the gravimetric determination of alumina in a sulphuric solution it must be remembered that these solutions often contain silicic, phosphoric, and arsenic acid, which are all carried down on precipitation with ammonia, along with a part of the sulphuric acid. Even on re-dissolving the ammoniacal precipitate in hydrochloric acid and re-precipitating with ammonia in presence of much ammonium chloride, the alumina may still contain as much as 2 per cent of sulphuric acid.

Determination of Alumina in Aluminates.—E. B.—This paper will be reproduced in full.

Titration of Soda in presence of Alumina, Vanadium, and Tungstic Acid.—E. B.

Leidenfrost's Experiment as the Foundation of a New Method of Evaporating Liquids of all kinds to Dryness without Loss.—E. Bohlig.—This memoir will be inserted at some length.

A Thermo-regulator with an Electrical Bell-Signal.—A. Kalecsinsky.—This paper requires the three accompanying illustrations.

Analyses of Damson Brandy and Brandy from Pressed Grapes from South Hungary and the adjoining Regions.—M. Petrowitsch.—A memoir of no general interest.

Does every Wine contain Tartar?—M. Petrowitsch.—The author shows that certain wines from Kalowitz, indisputably genuine, contain no potassium bitartrate.

Alkaline Reaction of Well-Waters.—M. Petrowitsch.—In the county of Bacs in Hungary the water of more than 100 wells gave a permanent red colour with rosolic acid. Even the waters of the Danube and the Theiss in this region (the Hungarian soda-district) yield the same reaction.

Separation of Gold and Platinum from Tin, Antimony, and Arsenic in Qualitative Reaction.—R. Fresenius.—This paper cannot be intelligibly reproduced without the accompanying illustration.

Determination of Arsenic and Boric Acid in Mineral Waters.—R. Fresenius.—The contents of two large flasks of the water were mixed with a little sodium hypochlorite to oxidise the ferrous carbonate present, and were then acidified with hydrochloric acid. A little more ferric chloride was added, and then pure precipitated calcium carbonate in excess. The whole was repeatedly mixed, and the ochreous precipitate formed was allowed to settle. Along with ferric hydroxide it contains all the arsenic and phosphoric acid. It is filtered, washed, dissolved in hydrochloric acid of sp. gr. 1.10, the solution is placed in a retort, ferrous chloride is added, and the whole distilled down to a small residue. To this there is again added hydrochloric acid of the same strength, the liquid is again distilled, repeating this operation until the last distillate is no longer rendered turbid by sulphuretted hydrogen. The distillates are mixed, and on treatment with sulphuretted hydrogen yield fine yellow arsenic sulphide. It is dried on a filter at 100°, washed with alcohol, carbon disulphide, and alcohol, and weighed. All the reagents are previously tested in a similar manner. If the residues of the distillations are evaporated down so as to eliminate silica, then treated with hydrochloric acid and water and the liquid repeatedly evaporated with nitric acid, the phosphoric acid may be at once precipitated as ammonia phosphomolybdate.

Determination of Boric Acid.—36,350 grms. water are mixed with sodium carbonate until the solution is distinctly alkaline, and are then strongly concentrated. The precipitate separated out, consisting chiefly of alkaline earthy carbonates and ferric hydroxide, is filtered off, washed, and as it still contains boric acid it is dissolved in hydrochloric acid, and this solution, after dilution with water, is again precipitated at a boil with potassium carbonate. The filtrate, separated from the precipitate, is now mixed with the former and evaporated down to a damp saline mass. The boric acid is liberated by acidulation with hydrochloric acid and extracted with alcohol at 95 per cent. In this manner there is obtained an alcoholic solution containing all the boric acid. It is mixed with an excess of potassa, distilled off, and evaporated down to a small residue. This is treated in a similar manner twice more, and the small saline mass ultimately obtained is treated with boiling water, separated by filtration from a residue consisting mainly of magnesium hydroxide, and which, after washing with boiling water, is dissolved in a little hydrochloric acid, and the solution is precipitated with potassa and a little potassium carbonate. Thus a filtrate is obtained free from all alkaline earths and containing all the boric acid along with potassium hydroxide and a little silica in the state of alkaline salts. From this solution the boric acid is separated according to A. Stromeyer's method.

Definition of Normal Solutions and on Cl. Winkler's Proposal for Re-organising the Volumetric System.—W. Fresenius.—This paper will be inserted at some length.

Rapid Separation of Slimy Precipitates.—K. Zulkowsky.—This can be effected in many cases by shaking up the liquid containing the precipitate with $\frac{1}{2}$ volume of ether. The ether entangles the precipitate and carries it to the surface, so that the clear aqueous solution can be withdrawn. The precipitate is then obtained on allowing the ether to evaporate.—(*Chemiker Zeitung*).

Apparatus for Opening up Minerals in a Current of Chlorine.—R. Schelle (*Berg. & Hüttenmänn Zeitung*).—This apparatus cannot be intelligibly described without the accompanying cut.

Spectroscopic Studies on Radiant Matter.—W. Crookes.—From the *Annales de Chimie et de Physique*.

Contribution to Quantitative Spectroscopic Analysis.—Gerhard Krüss.—The author has investigated the narrowest width of the ocular slit available in determining the coefficient of extinction. From his determinations it appears that the lowest admissible limit for the contraction of the slit (with the telescope used by the author having a magnifying of the eye-piece of 13.4) is 0.263 m.m. Thus, a spectral region of 3.524 m.m. is demarcated for the eye.

Vertical Polarisation Instruments.—H. Trannin, F. Schmidt, and Hænsch.—These appliances for the determination of sugar, described in *Dingler's Polyt. Journal* and in the *Zeitschrift für Instrumentenkunde*, are here briefly mentioned.

The Production of Hydrobromic Acid.—J. S. Stas.—The author gives a method for obtaining this compound, perfectly free from hydrochloric and hydriodic acids. For the details the reader is referred to the *Memoirs de l'Académie Royale des Sciences de Belgique*. The principle of the process is as follows:—The acid is evolved in the ordinary manner from red phosphorus, bromine, and water, but the bromine is previously freed from traces of chlorine and iodine by dissolving it in potassium bromide and distilling in contact with zinc oxide. The chlorine is converted into potassium chloride and the iodine is retained by the zinc oxide.

Determination of Traces of Sodium Chloride in presence of Potassium Chloride.—F. Röttger and H. Precht (*Ber. Deutsch. Chem. Gesellschaft*).—Twenty grms. of the finely powdered sample were covered in a beaker with 40 grms. alcohol at 90 per cent, often stirred with a glass rod, and after standing for half-an-hour mixed with $\frac{1}{2}$ c.c. of a 10 per cent solution of potassium carbonate, which is added drop by drop, stirring constantly, and decanted three times. The residue remaining insoluble is washed several times on the filter, the filtrate is evaporated down in a platinum capsule, the residue is gently ignited and weighed. In the residue the potassium chloride is determined with platinum chloride, and the sodium chloride is calculated as the difference. If a rapid determination of sodium chloride in a 98 per cent solution potassium chloride is required the following method is recommended:—20 grms. of the finely-powdered sample are placed in a flask graduated to 110 c.c. (10 c.c. correspond to the bulk of the potassium chloride taken) filled up to three-quarters with alcohol at 90 per cent by weight, often shaken, and after half-an-hour is added $\frac{1}{2}$ c.c. of a 10 per cent solution of potassium carbonate. The flask is filled up to the mark and shaken. When the liquid is clear 50 c.c. are drawn off with a pipette, evaporated down, and treated as above.

Sensitiveness of the Detection of Baryta or Sulphuric Acid.—Spencer Pickering.—From the *CHEMICAL NEWS*.

New Method for the Gravimetric Determination of Manganese.—H. von Jüptner (*Chemiker Zeitung*).—Already noticed.

Determination of Nitrous Acid in Nitrites.—L. P. Kinnicutt and J. U. Neff.—The authors modify the ordinary process as follows:—The nitrite in question is dissolved in at least 300 parts of cold water, and to this solution decinormal permanganate is added by degrees until the liquid takes a permanent red colour. Two to three drops of dilute sulphuric acid are added, and then an excess of permanganate. The dark red liquid is strongly acidified with sulphuric acid, heated to a boil, and the excess of permanganate is titrated back with decinormal oxalic acid.

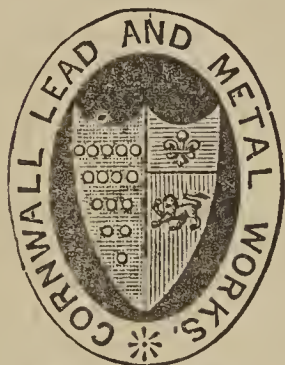
Appointment.—Dr. A. B. Griffiths, F.R.S. (Edin.), F.C.S., &c., Lecturer on Chemistry and Metallurgy at the Technical School, Manchester, has been appointed Head Master and Lecturer on Chemistry and Physiology at the New School of Science of the City of Lincoln.

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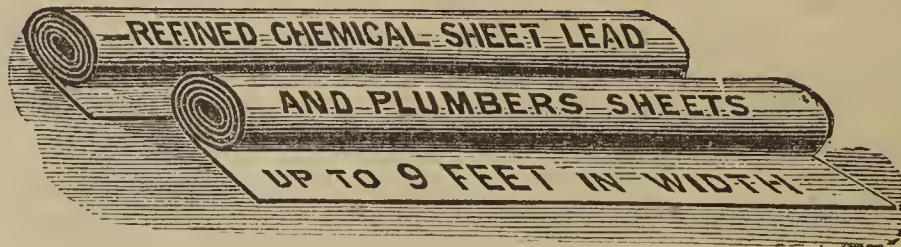
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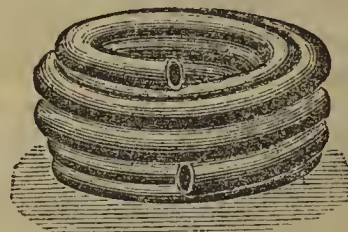
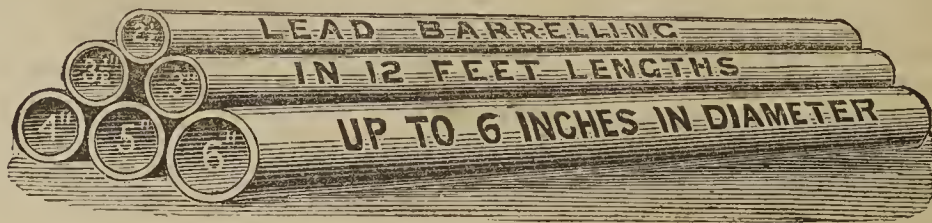
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THE CHEMICAL NEWS.

VOL. LIV. No. 1390.

NOTE ON THE ABSORPTION SPECTRUM OF DIDYMIUM.

By WILLIAM CROOKES,* F.R.S.

IN a paper on "Radiant Matter Spectroscopy" (Part 2, Samarium)* I said that in fractionation of the didymium earths with ammonia—"After a time a balance seemed to be established between the affinities at work, when the earths would appear in the same proportion in the precipitate and in the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them, when fractionation by ammonia could be again employed."

That in most methods of fractionation a rough sort of balance of affinities beyond which further separation by the same method is difficult, appears to be a general rule. I have long noticed this action when fractionating with ammonia, with oxalic and nitric acids, and with formic acid. The valuable point which renders this fact noteworthy is that the balance of affinities revealed by fractionation is not the same with each method. It was in consequence of the experience gained in these different methods of fractionation that I wrote in my paper read before the Royal Society, June 10th last (CHEMICAL NEWS, vol. liv., p. 13), after saying that I had not been able to separate didymium into Dr. Auer's two earths, "probably didymium will be found to split up in more than one direction according to the method adopted."

In illustration of this I may mention that, although I have not split up didymium into the two earths, or groups of earths, which are described by Dr. Auer, other processes of fractionation give me, so to speak, other cleavage planes or lines of scission through the compound molecule didymium.

According to Dr. Auer a line in the well-known yellow band, close to the soda line, but less refrangible (w. l. about 579), is a component of the absorption spectrum of neodymium, and therefore, under all conditions, its intensity should follow the same variations as the other bands of neodymium in the blue (wave-lengths 482, 469, 444). Some of my didymium fractions, however, show that the line 579 does not follow the same law as the other bands I have named. Thus in a rather low fraction (+ 6) of the didymium earths from gadolinite and samarskite I found that the neodymium line 579 was of the same degree of blackness as the adjacent praseodymium line in the yellow (wave-length about 571), but the bands in the blue of neodymium had almost disappeared. In the adjacent fractions of didymium I was enabled, by appropriate dilution, to keep this set of bands in the yellow as a standard, of exactly the same intensity; it was now seen that in successive fractions the intensities of the other more refrangible lines belonging both to neo- and praseodymium varied greatly from strong to almost obliteration, the bands in the yellow always being kept of the same intensity.

Didymium prepared from a specimen of fluocerite differed somewhat from the other didymiums. Here the band 579 (ascribed to neodymium) was very strong, the band in the yellow of praseodymium (571) slightly weaker, and the bands in the blue of neodymium (482, 469, and 444) easily visible. On diluting the solution the bands in the blue of neodymium and the one component of praseodymium in the yellow (571) appeared to follow the same law

in becoming fainter and fainter with dilution, whilst the other component band in the yellow of neodymium (579) remained unaffected.

It seemed to me that a possible explanation of this variation might be founded on the great strength of the bands in the yellow, and that the two fractions of didymium then under examination might differ only in the fact that one was slightly stronger than the other. To test this hypothesis I took the two fractions first experimented on, and putting each into a wedge-shaped cell of glass viewed them together in the spectroscope. *First*, I adjusted the wedges so that the group in the yellow appeared to be of the same intensity in each spectrum. On examining other parts of the spectrum it was seen that in one solution the bands in the green were tolerably strong and the bands in the blue scarcely visible, whilst in the other solution the bands in the green were very faint and those in the blue quite absent. *Secondly*, The position of the wedges was adjusted so that the bands in the green in each case should be of equal intensities. It was now seen that the alteration had greatly upset the balance of the bands in the yellow, the solution in which the bands in the green were faintest before now having much stronger yellow bands than the other. The explanation mentioned above therefore falls through, and I see no other way of accounting for the facts except on the supposition that by the mode of fractionation then adopted didymium had split up in a different manner to what it would have done if the method of Dr. Auer had been followed.

The colour of the different fractions of didymium nitrate varies from a dark rose-red at the more basic end (+ 17) to amber at the less basic end (+ 4). These variations in colour do not necessarily accompany a difference in the absorption-bands, for in one instance an amber and a rose-coloured salt were found to have almost identical spectra.

It would almost appear from these experiments, coupled with the facts I brought forward in last week's CHEMICAL NEWS (p. 14), that the "one band, one element" theory I lately advanced in connection with the phosphorescent spectrum of yttrium, may probably hold good in the case of the group of elements forming absorption spectra. According to this hypothesis, therefore, neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules into which the complex molecule didymium splits up by one particular method of fractionation.

ON THE ALLEGED REDUCTION OF FERRIC NITRATE BY MERCURY.

By GEORGE LUNGE.

MR. THOMAS BAYLEY asserts (CHEMICAL NEWS, vol. liv., p. 6) that ferric salts are reduced to ferrous salts in contact with mercury, and that therefore a "dark colour" or "pink to reddish tints" are produced when shaking acid containing iron in the nitrometer. After the experiment the liquid is stated to give a blue colouration with potassium ferricyanide.

I have tried this experiment, but I have failed to discover any reduction to ferrous salt. In the presence of a comparatively large quantity of ferric nitrate the liquid within the nitrometer assumed a raspberry tint, but never that well-known chocolate colour of a solution of NO in FeSO₄. The same liquid, after being diluted and partly neutralised with ammonia, and cooled down, gave no reaction with potassium ferricyanide. Of course, if the liquid were treated with that reagent just after being diluted, and therefore quite hot and containing an enormous excess of acid, it would turn blue with potassium ferricyanide; but no one acquainted with qualitative analysis will work that way.

* Phil. Trans., Part 2, 1885, p. 706. A Reprint of this paper is also commenced in this No. of the CHEMICAL NEWS, p. 28.

In another experiment I purposely added less ferric nitrate to the nitrous vitriol, but sufficient to give a very strong reaction with potassium sulphocyanide after diluting and cooling. In this case no colour whatever was observed in the nitrometer. The above quantity is more than I have found in ordinary commercial nitrous vitriol. That any commercial nitrous vitriol should contain sufficient iron, in *any* shape, to dissolve a measurable quantity of NO, is an assumption for which no proof has been given, and which I shall not stop to discuss, having closed my account in this matter.

Zürich, July 8, 1886.

ON THE ESTIMATION OF CAUSTIC AND CARBONATED ALKALI IN PRESENCE OF EACH OTHER.

By H. JOSHUA PHILLIPS.

THE usual method, which involves two separate determinations of Na_2O in order to obtain the ratio of Na_2O present as hydrate to that present as carbonate, the author has found may be estimated fairly accurate in one and the same portion of sample taken. The method adopted depends upon the fact that recently precipitated BaCO_3 requires the same amount of normal acid to dissolve it as it would take to neutralise its equivalent of Na_2CO_3 in solution. One grm. (or more if the percentages are low) of the sample is taken and dissolved in a flask with 150 c.c. of distilled water, which has been recently boiled in order to eliminate any CO_2 that may be present. A clear solution of baric chloride is now added in just sufficient quantity to completely precipitate all the combined CO_2 ; it is then heated to incipient ebullition, and allowed to cool with the flask covered. After perfect precipitation of the baric carbonate has been insured, a few drops of an alcoholic solution of phenolphthalein are added, and the whole thoroughly mixed. NHCl is now run in gradually from a burette (stirring) until the last drop completely decolourises the solution, and the volume required noted. The NHCl is then run in until the whole of the baric carbonate is just dissolved, and then a few c.c. added in excess, the total volume used being noted. The excess of HCl is titrated back with normal Na_2CO_3 (boiling when near the neutral point to eliminate CO_2) until the pink tint is developed. The total quantity of normal acid used, minus the volume used for the neutralisation of the hydrate, will leave the quantity of acid equivalent to the carbonate present in the sample. Sulphuric acid is inadmissible in the titration, unless the theoretical quantity of baric chloride was used. In commercial lyes, sulphates being present, the whole of the precipitate produced by the BaCl_2 will not dissolve; but the BaCO_3 being not so fine as the BaSO_4 , it will be readily discerned when the former has disappeared.

Coincident results have been obtained by this method to that quoted by Sutton in his "Volumetric Analysis," who also states that, after the hydrate has been determined in an aliquot part of the clear solution, the carbonate may be filtered off and titrated with nitric acid.

1, Park Place, Tredegar, Mon.

Determination of Santonine.—Ehlinger.—(*Chemiker Zeitung*). The author boils the plant repeatedly with $\frac{1}{2}$ part slaked lime and abundance of alcohol at 0.935 sp. gr., distils off the bulk of the alcohol, and saturates the residual liquid with carbonic acid. The filtrate immediately freed from the calcium carbonate is evaporated to dryness and the residue is boiled with alcohol at 0.935 sp. gr., with the addition of animal charcoal. On expulsion of the alcohol the filtrate yields santonine in white crystals.—*Zeit. ch. f. Anal. Chemie*.

ON RADIANT MATTER SPECTROSCOPY.*

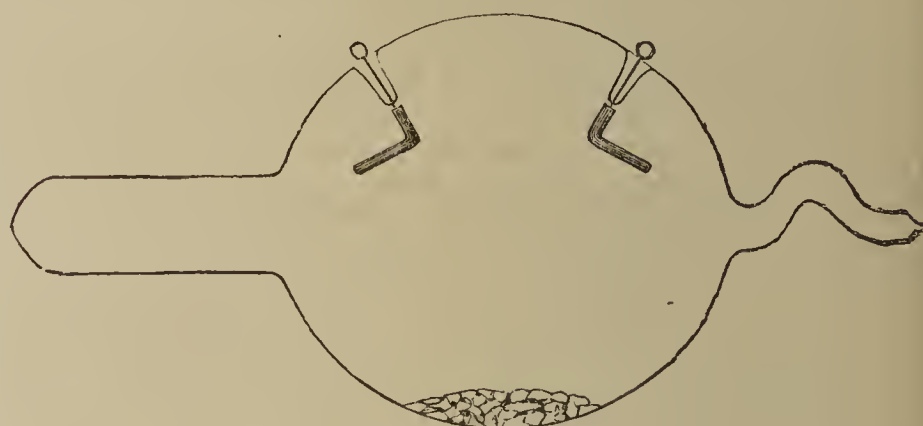
PART II.—SAMARIUM.

By WILLIAM CROOKES, F.R.S.

Introduction.

90. IN the concluding sentence of the Bakerian Lecture which I had the honour to deliver before the Royal Society, May 31, 1883, I said that the new method of Radiant Matter Spectroscopy there described had given me not only spectrum indications of the presence of yttrium as an almost invariable, though very minute, constituent of a large number of minerals, but had likewise revealed signs of another spectrum-yielding element. I stated that I had repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band. That this second spectrum was not then new to me is shown by a paper sent to the Royal Society in 1881,† in which I described a double orange band occurring in the phosphorescent spectrum of an earth less frequently met with than the "pale yellowish coloured earth" (since identified as yttria) which gave me the "red, orange, citron, and green bands."

FIG. 1.



91. The method adopted to bring out the orange band is to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness. It is then put into a radiant-matter tube, of the form shown in Fig. 1, and the induction spark is passed through it after the exhaustion has been pushed to the required degree. The anhydrous sulphate thus left frequently shows the orange band in the radiant-matter tube, though before this treatment the original substance shows nothing.

The Elimination of Mercury Vapour from Vacuum Tubes.

92. The presence of mercury vapour is liable to interfere with the spectrum indications, and when working in an entirely new field, where the mutual reaction of bodies one on the other is the subject of the research, it is always desirable to reduce the unavoidable constants to a minimum. In a tube exhausted in the ordinary manner by the Sprengel pump more mercury vapour is present than is generally supposed. Unless the tube is exhausted and sealed off without loss of time, mercury diffuses through the connecting tubes, and soon gets into the vessel under experiment. It is not easily detected by the spectroscope so long as the tube remains cold, but when the passage of the current has warmed the glass and the metal poles the mercury lines become distinctly visible, and the same result is obtained at once when the tube is heated by a lamp.‡

* A Paper read before the Royal Society, June 18, 1885.

† *Proc. Roy. Soc.*, vol. xxxii. (1881), p. 206.

‡ In incandescent lamps exhausted by means of a mercury pump, a peculiar blue phosphorescence is observed to fill the globe when the filament is raised much above its normal incandescence. This phenomenon has been examined and discussed by Mr. Edison in America and by Mr. Preece in England (*Proc. Roy. Soc.*, vol. xxxviii., No. 236, p. 219). During the course of my work on the manufacture of incandescent lamps I have frequently noticed the same effect. Examined

The following experiment illustrates this behaviour of mercury:—A small radiant-matter tube, having flat aluminium poles connected to platinum terminals passing through the glass, was sealed to the pump and quickly exhausted. An induction current was immediately passed through, and the light examined in the spectroscope. No mercury lines were detected. The tube was then heated strongly, the spectroscopic examination being continued: no mercury lines were seen. The apparatus was then allowed to rest for a day, and the experiments were repeated. In the cold no mercury lines could be seen, but on heating the tube they became distinctly visible.

93. The tube was then exhausted to the highest possible point, and sealed off. In the cold it was impossible to get an induction-spark through the tube,—it was absolutely non-conducting. However, on heating the tube with a Bunsen flame, keeping the coil going all the time, suddenly the current passed, lighting up the inside of the tube with a greenish blue light, in which the spectroscope showed strong mercury lines. On allowing the tube to cool it again became non-conducting, and the experiment could be repeated.

This shows that in a vacuum tube which is so highly exhausted as to be non-conducting there is plenty of mercury present to carry an induction current, only it is not in the form of vapour, but is condensed on the metallic poles or on the sides of the glass.

94. It is much more difficult than is generally supposed to keep mercury vapour from diffusing itself into the experimental tubes. Gold-leaf was packed loosely in a tube about 2 feet long, which was then interposed between the pump and the radiant-matter tube. This answered for a short time, but whilst it certainly kept back some of the mercury, it let much through.

For a long time I used a tube about 2 feet long, packed with coarsely-powdered sulphur. This is effectual at first, but there is a liability of sulphur vapour getting into the tube, and this might be as disastrous as mercury. The sulphur was therefore kept out by interposing another tube containing finely-divided copper. This, however, was not quite effectual: after a time mercury was found to have run the gauntlet of both sulphur and copper. It is of no use trusting to a solid reagent to absorb a gaseous body. Where the gas and solid meet there may be action, but some of the gaseous molecules are sure to get through without coming within the solid's sphere of attraction.

95. I finally adopted the following plan, which answers perfectly so far as my experiments have yet gone:—Sul-

phur is first prepared by keeping it fused at a high temperature till bubbles cease to come off, so as to get rid of water and hydrogen compounds. It is then allowed to cool, and is then pounded and sifted so as to get it in the form of granules averaging a millimetre in diameter. A glass tube, a centimetre in diameter and about 2 feet long, is lightly packed for half its length with this sulphur, and next about 2 inches of iodide of sulphur (I_2S_2) is added, and the rest of the tube is then filled up with sulphur. Ignited asbestos is packed in at each end to keep the sulphur from blowing out whilst the vacuum is being made, or from being sucked through when air is suddenly let in. This contrivance entirely keeps mercury vapour from passing through, since the iodide of sulphur holds its iodine very loosely, and fixes the mercury in the form of non-volatile red iodide. A glass tube containing finely-divided copper must follow in order to keep sulphur out. With this blockade interposed between the pump and experimental tubes I have been unable to detect mercury vapour in any of the tubes, whether in the cold or on heating them.

Mixed "Citron" and "Orange" Spectra.

96. Since the date of my last paper I have devoted myself to the task of solving the problem presented by the double orange band first observed in 1881. With the yttrium experience as a guide it might be thought this would not be a difficult task, but in truth it helped me little beyond increasing my confidence that the new, like the old, spectrum was characteristic of an element. The extreme sensitiveness of the test is a drawback rather than a help. To the inexperienced eye one part of "orange band" substance in ten thousand gives as good an indication as one part in ten, and by far the greater part of the chemical work undertaken in the hunt for the spectrum-forming element has been performed upon material which later knowledge shows does not contain sufficient to respond to any known chemical test. It is as if the element sodium were to occur in ponderable quantity only in a few rare minerals seldom seen out of the collector's cabinet. With only the yellow line to guide, and seeing the brilliancy with which an imponderable trace of sodium in a mineral declares its presence in the spectrum, I venture to think that a chemist would have about as stiff a hunt before he caught his yellow line as I had to bring my orange and citron bands to earth.*

Chemistry, except in few instances, as water-analysis and the detection of poisons, where necessity has stimulated minute research, takes little account of "traces;" and when an analysis adds up to 99.99, the odd 0.01 per cent is conveniently put down to "impurities," "loss," or "errors of analysis." When, however, the 99.99 per cent constitutes the impurity and this exiguous 0.01 is the precious material to be extracted, and when, moreover, its chemistry is absolutely unknown, the difficulties of the problem become enormously enhanced. Insolubility as ordinarily understood is a fiction, and separation by precipitants is nearly impossible. A new chemistry has to be slowly built up, taking for data uncertain and deceptive indications, marred by the interfering power of mass in withdrawing soluble salts from a solution, and the solubility of nearly all precipitates in water or in ammoniacal salts when present in traces only. What is here meant by "traces" will be better understood if I give an instance. After six months' work I obtained the earth didymia in a state which most chemists would call absolutely pure, for it contained not more than one part of impurity in five hundred thousand parts of didymia (131). But this one part in half a million profoundly altered the character of didymia from a radiant-matter-spectroscopic point of view, and the persistence of this very minute quantity of interfering impurity entailed another six

in the spectroscope the phosphorescent light filling the globe shows the mercury lines strongly. In order to examine this phenomenon more closely the following experiments were tried:—An incandescent lamp with fine carbon filament which had been plated up in vapour of carbon tetrachloride was placed in one of the sides of a Wheatstone bridge and connected with a dynamo-electric machine, where by means of a suitable rheostat it could be raised to any desired degree of incandescence. A spectroscope was adjusted so that the slit was opposite the rarefied space between the two limbs of the filament. With an E.M.F. of 64.5 volts, a current of 0.97 ampère, and a light of twenty candles, no lines were visible in the spectrum; on increasing the volts to 73.6 the current became 1.15 ampères, and the c. p. 43. At this stage flashes of blue phosphorescence filled the bulb at regular intervals of about ten seconds, and at the same instant the mercury lines were seen in the spectroscope, $\frac{1}{\lambda^2}$ 2984, 3006, 3354, and 5265 being most prominent. On increasing the E.M.F. to 81.3 volts the current became 1.28 ampères, and the light seventy-four candles; the flashes of phosphorescent light became more frequent, pulsating very regularly once every three seconds, and at each flash showing the mercury spectrum strongly. The E.M.F. was next increased to 99.7 volts, and the ampères to 1.83; at this point the light was equal to 172 candles. The flashes of light became more and more frequent, rising quickly from once in two seconds till they occurred too rapidly to count, and the blue phosphorescence became continuous and seemed to fill the globe. The mercury spectrum at this stage was permanent, and most of its lines could be detected. The flashes of light were probably owing to some such action as this:—The hot filament offering a considerable resistance to the passage of the current, the long length of insulated wire in the circuit (about half a mile, including the lamps used for house-lighting) charged up like a condenser, and then at intervals discharged through the highly rarefied vapour in the bulb.

* So recently as the year 1880 a high authority on blowpipe chemistry seriously argued that the yellow-coloured flame "which is ascribed to sodium" is not caused by that metal, but is due to "chemical water."—(CHEMICAL NEWS, vol. xli., p. 159, April 2, 1880),

months' extra labour to eliminate these final "traces" and to ascertain the real reaction of didymia pure and simple (131).

For a long time the "citron-band" and the "orange-band" spectra were confounded. That they were due to two different states or kinds of matter was not easily decided, since in all the early experiments I was dealing with a mixture; consequently the spectra obtained were not only mixed, but differed considerably in the relative intensities and faintness of the different lines (146).

97. At last having separated yttria and obtained its spectrum pure (71), the characteristic lines in the other spectrum or spectra could be provisionally mapped out by difference, and a systematic hunt was instituted for the new "orange-band" substance, which to avoid periphrasis was termed α . Naturally my thoughts turned to samarskite and the yttria earths. A wide, prolonged survey over every available substance had convinced me that the number of bodies giving a discontinuous phosphorescent spectrum is extremely limited, and to be counted on the fingers of one hand; and having satisfactorily mated one of these spectra to yttria it became in the highest degree probable that the twin spectrum should belong to one of the nearest chemical associates of yttria.

Chemistry of the "Orange-band" forming Body.

98. At first it was necessary to take stock, as it were, of all the facts regarding α which had turned up during the search for the orange band. In the first place α is almost as widely distributed as yttria, generally occurring with the latter earth. Sometimes, however, the orange band was strong where the citron band was almost or quite absent. It is almost certainly one of the earthy metals, as it occurs in the insoluble oxalates, in the insoluble double sulphates, and in the precipitate with ammonia. It is not precipitated by sodic thiosulphate, and, moreover, it must be present in very minute quantities, since the ammonia precipitate is always extremely small, and as a rule α is not found in the filtrate from this precipitate.

99. At this stage of the enquiry the chemical reactions of α were much more puzzling than with yttria. At the outset an anomaly presented itself. The orange band was prone to vanish in a puzzling manner. Frequently an accumulation of precipitates tolerably rich in α was worked up for purposes of concentration, when the spectrum reaction suddenly disappeared, showing itself neither in precipitate nor filtrate (3, 101, 108, 115); whilst on other occasions, when following apparently the same procedure, the orange band became intensified and concentrated with no apparent loss. The behaviour of the sulphate to water was also very contradictory; on some occasions it appeared to be almost insoluble, whilst occasionally it dissolved in water readily (115).

100. For some time I debated whether the orange-band spectrum might not be a mere modification of the yttrium spectrum induced by the presence of some extraneous body. We know that yttria *per se* has little or no phosphorescence (75), that this power chiefly resides in the ignited sulphate. Might it not happen that some other earth with molecules peculiarly sensitive to the longer vibrations would confer upon yttria some of its sensitiveness to the red end of the spectrum?

It would be too much like a repetition of my paper on the yttrium spectrum quest were I to detail the numerous experiments and false starts with samarskite, orangite, thorite, strontianite, coelestine, perofskite, cerite, coral, &c.; but I may be permitted to extract from an enormous mass of chronicles which must remain unpublished, some few experiments which will usefully emphasize what I may call the nodal points in this research.

"X" from Samarskite.

101. It was to be expected that samarskite would contain α . It occurred, however, very little in the yttria group, but was found with the decipia residues (47, 49), or

the earths forming, with potassium, insoluble double sulphates,—ceria, lanthana, didymia, decipia, samaria, together with a little thoria and zirconia. These residues were dissolved in hydrochloric acid, precipitated with ammonia, washed till free from potassic salts, re-dissolved, and precipitated as oxalates. The filtrate was set aside in Winchester quart bottles, and after standing for some weeks a further quantity of insoluble oxalates was found deposited at the bottom of the bottles. These were collected, and appeared to be very rich in α ; but on attempting to work them up vexatious anomalies constantly started up: suddenly the orange band would disappear, and, after being lost sight of for a week or two, would return in a manner equally unaccountable (3, 99, 108, 115).

Thorite and Orangite.

102. Early in my research thorite and orangite (26) had given a brilliant spectrum, afterwards identified with that of yttria (70). When hunting for α some of the insoluble double sulphates from these minerals (32) were treated like the samarskite double sulphates to remove potassium (101), and examined in the radiant-matter tube. Here, also, was found the orange-band spectrum, quite different from the yttrium spectrum of the soluble sulphates; but, as usual, it behaved in a most capricious manner.

Perofskite.

103. An American friend, Mr. George F. Kunz, with great kindness sent me some pounds' weight of the rare mineral perofskite (calcic titanate) in fine crystals, from Magnet Cove, Arkansas, together with a large number of specimens of associated minerals from the same locality. The perofskite was found to be richer in α than any mineral yet examined. At great sacrifice of material a small portion of an earthy body was obtained giving the orange-band spectrum more brilliantly than I ever had seen it before. Analysis failed to detect anything in it but lime (5, 9), the flame spectrum showed lime, and the atomic weight came out $RO = 55.3$, CaO being 56.

Calcite.

104. Mr. Lettsom, understanding I was engaged in quest of an unknown body supposed to be associated with calcium, most kindly sent me specimens of rare and curious minerals; and through his good offices Professor Albin Weisbach presented me with an extensive set of calcites; these, prior to the invention of the spectroscope, had been measured by Professor A. Breithaupt, who, owing to the discordant measurements, held what is known as "calcium" to consist of two or more allied elements, which as yet chemists were unable to separate.

These calcites were treated as usual, and examined most carefully in the radiant-matter tube. In one of them only was a trace of yttria found, but the orange-band spectrum was very faintly seen in six of the thirteen specimens. The others shone with the usual greenish blue phosphorescence of calcic sulphate, giving no lines or bands in the spectrum.

I am also indebted to M. Lettsom for a specimen of calcite from Branchville, S. Carolina, which, when heated, has the curious property of glowing strongly with a golden yellow light showing a faint continuous spectrum. In the radiant-matter tube the phosphorescence was very brilliant, but there was no discontinuity in the spectrum, only a concentration of light in the red portion.

Dolomite.

105. Another curious mineral, for which I am also indebted to Mr. Lettsom, is a granular dolomite from Utah. When scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it Hell-fire Rock. By itself in the radiant-matter tube it brightly phosphoresces with a reddish light, showing no bands, but a concentration of light in the red. Treated with sulphuric acid in the usual manner, and then

examined in a vacuum tube, a similar continuous spectrum was observed. Chemical analysis showed that it was a nearly pure double calcic and magnesian carbonate, with a little iron, alumina, and phosphoric acid.

Amongst other minerals found to give the orange-band spectrum I may mention zircon, euxenite, tyrite, fergusonite, rhabdophane, cerussite, apatite, galliferous blende, argentiferous galena, anglesite, harmotome, allanite, cerite, magnesite, oolite from Bath, &c.

Coral.

106. In my former paper (88) I mentioned that a specimen of pink coral contained about a half per cent of yttria, judging from the very strong yttrium spectrum it gave in the vacuum tube. Professor Martin Duncan has identified this specimen as a *Gorgonia* of the genus *Melithæa*. Another recent coral, *Mussa sinuosa*, gave equally strong indications of yttrium. By the kindness of Professor Duncan I have since been enabled to submit a large number of corals to spectrum examination in the radiant-matter tube. Nearly all showed more or less discontinuity in their phosphorescent spectra, but as in the yttrium spectrum research I obtained only two specimens giving a brilliant yttrium spectrum, so in the present quest I have found only two corals giving a strong orange-band spectrum. One is a *Pocillopora damicornis*, from Singapore and most of the Pacific Islands which have reefs, one of the old group of tabulate corals. A fragment of this coral, treated with sulphuric acid and examined in the radiant-matter tube, gave as brilliant an orange-band spectrum as I had ever seen. The other is of the species *Symphyllia*, close to *Mussa*, a reef-builder from the same locality as the *Mussa* which gave so much yttria.

Sea-water.

107. These results induced me next to try sea-water. Ammonic oxalate and hydrate gave a white precipitate, which was filtered off and washed. The oxalate was then ignited, dissolved in nitric acid, and the solution supersaturated with ammonia and boiled. The resulting precipitate, tested in the radiant-matter tube, showed the orange-band spectrum very well.

"X" in Strontium Minerals.

108. The orange-band spectrum in the radiant-matter tube at first sight bore a close resemblance in the red region to the flame spectrum of strontium; the two spectra therefore were examined together, and on comparing them a near coincidence was observed between two lines in the orange. Was it possible that the sought-for element was strontium?

This led to an examination of the strontic nitrate used in the flame reaction. When converted into sulphate and tested in the radiant-matter tube the experiment succeeded only too well. The orange-band spectrum came out brilliantly.

Other commercial strontium compounds were now tested. Yttria was found almost universally, but the orange band was capricious; the nitrate generally showed it well, caustic strontia sometimes, chloride as a rule not at all. These were from different makers. The source was enquired for, and in a few weeks my laboratory was filled with large specimens of Gloucestershire, Italian, and Sicilian celestine, and Scotch, Italian, and German strontianite, together with waste-products, mother-liquors, and every commercial salt of strontium. The kindness of the manufacturers was great, and I regret that the outcome was not more notable.

Italian celestine showed a good orange-band spectrum when crushed and examined in the tube without any chemical treatment. After getting the mineral into solution by fusion with sodic carbonate, &c., the x could be concentrated by fractionally precipitating with alkaline carbonates (coming down in the first fractions). The sulphate produced from this precipitate also showed the desired spectrum.

This sulphate was digested for some time in warm ammoniac carbonate, and now the old distressing anomalies recommenced. On most occasions, when working roughly on a scale of a few grammes, all the x was found in the filtrate on evaporation and ignition. When, however, I took identically the same material, and worked it up more carefully, in pounds or hundredweights, it sometimes gave nothing at all, sometimes only a *ridiculus mus* on the smallest-sized filter, got from a mountain of raw material. This was at first accounted for by the want of homogeneity of the mineral. The real explanation, however, was not discovered till long after (115).

A quantitative estimation was attempted of the amount of x substance got from Italian celestine: 630 grms. gave 1.525 grms., or 0.24 per cent. Analysis showed this to be chiefly strontic sulphate, and the atomic weight of the metal was close to that of strontium.

(To be continued.)

THE AMOUNT OF MOISTURE WHICH SULPHURIC ACID LEAVES IN A GAS.

By EDWARD W. MORLEY.

BERZELIUS and Dulong,* about 1820, and Erdmann and Marchand,† about 1842, employed calcium chloride in determining the atomic weight of oxygen, and were probably not aware that it leaves unremoved a comparatively large amount of water. Dumas,‡ in 1842, and Pettenkofer,§ in 1862, mentioned as well known, the fact that calcium chloride will not dry a gas as completely as sulphuric acid. Favre,|| in 1844, proved that sulphuric acid at ordinary temperatures dries a gas so completely that neither sulphuric acid at -17° C. nor phosphorus pentoxide will absorb a sensible quantity of moisture from 40 litres of gas, nor even from volumes "bien plus considérables." He also attempted¶ in a most ingenious way to determine whether a gas dried by either of these agents was absolutely dry. He passed air dried as perfectly as possible over red-hot copper, and then again through a drying tube. In one experiment, 148 litres of air were reduced to 117 litres of nitrogen, and deposited 0.0025 grm. of water; in the other, 110 litres of air were reduced to 87 litres of nitrogen, and deposited 0.0015 grm. of water. Hence he concluded that a litre of gas dried by sulphuric acid or phosphoric oxide contained not more than 0.00006 or 0.00008 grm. of water.

He also proved** that no other force than the tension of the vapour of water causes it to be retained in certain gases. Favre further proved,†† as did Regnault in 1845,‡‡ that drying tubes of no large dimensions are required to utilise the whole drying power of the drying agent with which they are filled. In 1864, and again in 1865, Fresenius§§ published experiments, which, if they were affected by no source of error at that time unsuspected, would show that sulphuric acid leaves one or two decimilligrams. of moisture in a litre of gas. But in 1876, Dibbitts||| published experiments in which precautions were taken against the leakage of moist air through caoutchouc connectors, which showed that 308 litres of air dried by sulphuric acid at ordinary temperatures gave up but 7 decimilligrams. of moisture to phosphorus pentoxide.

Dibbitts also proposed a method for solving the remain-

* Ann. Chim. Phys., 2nd Series, vol. xv., p. 388.

† Journ. Prakt. Chemie, vol. xxvi., p. 464.

‡ Ann. Chim. Phys., 3rd Series, vol. viii., pp. 193, 210.

§ Lieb. Ann. Supp., vol. ii., p. 29.

|| Ann. Chim. Phys., 3rd Series, vol. xii., p. 223.

¶ Ibid., vol. xii., p. 225.

** Ibid., vol. xii., p. 227.

†† Ibid., vol. xii., p. 228.

‡‡ Ibid., vol. xv., p. 152.

§§ Zeitschr. Anal. Chem., vol. iv., p. 180.

||| Ibid., vol. xv., p. 160.

ing question: How much moisture is left in a gas dried by phosphorus pentoxide? He proposed to evolve a gas of which we might be certain that it contained no water, to pass it into water, and then to dry it with phosphorus pentoxide. He suggested the evolution of dry oxygen by heating fused potassium chlorate. Whether perfectly dry oxygen could be thus obtained remains to be seen; the task of keeping up a suitable current of oxygen till a few hundred litres shall pass the absorption tubes would involve a good deal of labour.

Desiring to know the amount of water which sulphuric acid or phosphorus pentoxide fails to remove from a gas, I succeeded in devising a method which has made the solution of the problem easy. It permits the determination of the absolute amount of moisture left in a gas by any drying agent; the maintaining a slow current of air for days or weeks demands attention for only some five minutes each day, so that very large volumes of air may be used, at small velocities, and even if the residual moisture is as little as a hundredth or a thousandth of a milligram. in a litre, it may be determined with any needed accuracy.

I devised the method with the intention of applying it first to phosphorus pentoxide. But in the third number of the *Zeitschrift für Analytische Chemie* for 1884, Mathesius made certain statements about the use of sulphuric acid in drying tubes, in consequence of which I first undertook the study of the absolute amount of moisture left in a gas by this drying agent.

The paper of Mathesius raised a preliminary question which had to be answered. He found that certain drying tubes filled with sulphuric acid, of specific gravity 1.84, when used to absorb moisture as in organic analysis, lost weight at the rate of five or more decimilligrams. an hour. This statement must be taken as referring to sulphuric acid supposed to be pure; because a statement that impure sulphuric acid contained some volatile impurity would hardly be worth publication; and also because, in order to lessen the loss of weight in his drying tubes, Mathesius diluted the acid somewhat, probably supposing that the vapour of sulphur trioxide escaped and occasioned the loss of weight.

It is difficult to believe that either water or sulphur trioxide can be given up by pure sulphuric acid to a current of gas in any such quantity as Mathesius observed. Regnault* determined the tension of the vapour of water given off at 20° C. by sulphuric acid of the formula $\text{SO}_3 + 2\text{H}_2\text{O}$. This is 0.15 m.m., so that a litre of absolutely dry air passing through such acid would take up at this temperature 0.16 milligram. of water. He gives no results for acid more concentrated than this; but from a comparison of the results for more dilute acids it is difficult to believe that an acid containing half a molecule of water and one molecule of the monohydrated acid would give up to a litre of absolutely dry air as much as the twentieth of a milligram. of water at ordinary temperatures.

And as to the evaporation of sulphur trioxide from sulphuric acid: Dumas† passed 20 litres of air through pure sulphuric acid, and into solution of barium chloride, which preserved "une limpidité absolue." But if the loss of weight observed by Mathesius was due to the escape of sulphur trioxide, Dumas should have obtained not only a visible but a weighable precipitate.

But while we may dismiss the idea that sulphur trioxide escapes from sulphuric acid in drying tubes in ordinary conditions in any such quantities as several decimilligrams. an hour, it was necessary for the determination of the absolute amount of moisture left unabsorbed by sulphuric acid that the amount of sulphur trioxide volatilised should be accurately determined. For this purpose I made several experiments. In one of them, a wash-bottle and a Winkler's absorption tube were filled with pure sulphuric acid. This acid I dis-

tilled from a pure acid, rejecting the first and the last fifth. Its specific gravity at 22° and at 16.8° C., compared with water at 4°, weights being reduced to a vacuum, and the thermometer being corrected for error of zero point, was found to be 1.8344 and 1.8394. A current of air was aspirated through a gas-meter, through the wash-bottle of acid, through the absorption tube with acid, through an empty tube two metres long, through a plug of glass-wool, and through an absorption tube with pure water. The acid in the absorption tube occupied about two metres and a half; the water in the other absorption tube occupied about a metre. The parts of the apparatus were fused together. When 6800 litres had passed, not too rapidly, the sulphuric acid in the water was determined as barium sulphate, and found to be 3.1 milligrams. In a second experiment at a somewhat lower temperature, 0.7900 litre were passed and 2.5 milligrams. of acid were found in the second absorption tube. Several experiments were made in which air passed, at the rate of two litres an hour, into a solution of barium chloride; in which experiments neither myself nor Dr. Spenser, my assistant, could detect any trace of a precipitate till the third day.

With the degree of approximation thus far obtained, therefore, we may conclude that a litre of air passed through sulphuric acid of the specific gravity of 1.84 will take up something like the two-thousandth or three-thousandth part of a milligram. of sulphur trioxide at ordinary temperatures.

This being determined, the way was clear to determine the absolute amount of moisture left in a gas by sulphuric acid. To Liebig's potash bulbs I fused a sixth bulb, connected with the others by a capillary tube of so small bore that when a vacuum was maintained at one end, one or two cubic centimetres of air would pass through it in a minute. In this sixth bulb I placed sulphuric acid so diluted with water that air passing through it would take up a certain small amount of water. In the bulbs which belonged to the original apparatus was placed sulphuric acid of specific gravity 1.8381 at 18° C., compared with water at 4° C., weights and thermometer being corrected.

In use, a partial vacuum was maintained in the five bulbs containing strong acid, while the dilute acid was in contact with air at ordinary pressure. Air in passing from the dilute acid through the constriction towards the strong acid would therefore expand a number of times depending on the pressure in the partial vacuum. The air before entering the dilute acid was made as dry as sulphuric acid can render a gas; it took up water from the dilute acid; it was expanded; the increased volume was made as dry as sulphuric acid can render a gas.

Let us imagine, for the sake of clearness, that the expansion in passing the constriction was ten times, that five litres of air entered the dilute acid, and that therefore fifty litres passed out of the strong acid. Let us also make two alternative suppositions in order; first, that sulphuric acid makes a gas perfectly dry, and second, that it leaves a hundredth part of a milligram. of water in a litre of gas.

If, according to the first supposition, sulphuric acid makes a gas perfectly dry, the five litres of dry air which enter the six-bulb apparatus carry into it no water. In the sixth bulb they take up a small quantity of water. Passing the constriction, they become fifty litres. The sulphuric acid makes the fifty litres perfectly dry, and no water is carried out of the apparatus. Therefore the only effect changing the weight of the apparatus is the escape of sulphur trioxide, the amount of which is approximately known.

But, secondly, if sulphuric acid leaves a hundredth of a milligram. of water in a litre of gas, the five litres of air entering the apparatus carry into it one-twentieth of a milligram. of water. In the sixth bulb, more water is taken up. The five litres expand to fifty. Now the drying such a gas as air is simply a process of reducing the vapour tension of the accompanying vapour of water. One litre of air dried by sulphuric acid will contain water

* *Ann. Chim. Phys.*, 3rd Series, vol. xv., p. 179.
† *Ibid.*, 3rd Series, vol. iii., p. 204.

possessing a certain tension, whatever be the pressure of the air. At least Regnault proved this to be true within one per cent. The fifty litres of air will therefore carry out ten times as much moisture as the five litres brought in. Neglecting for a moment the evaporation of sulphur trioxide, the apparatus will lose nine-twentieths of a milligram. in weight. Conversely, if we knew the expansion to be ten times, and the entering air to be five litres, and the loss of weight to be 0.45 milligram., we could compute the water remaining in each litre to be 0.01 milligram.

In applying this principle, it was necessary to avoid errors due to leakage of moist air into the apparatus during the long time through which an experiment lasted, and to provide for weighing the six-bulb apparatus so accurately as to make certain the detection of a total effect of a few tenths of a milligram. I secured sufficient accuracy in weighing by using as a counterpoise an apparatus of the same shape and same kind of glass, filled with the same acid, and interposed in the same current of air. To these I fitted ground glass caps as accurately as I could, so that I could leave the two apparatus on the balance for several days without any change in their relative weights; of course after applying corrections for the state of the barometer and thermometer.

I also fitted to the two apparatus just named, a third, which prevented the diffusion of moist air backward from the vacuum, and a fourth which dried the air before it entered the first and second apparatus, all, to each other, by glass tubes with joints carefully ground which were made tight with a fat from which all matter volatile at common temperatures had been removed. In this way, I could leave the apparatus for weeks with the certainty that moist air could not enter the apparatus.

The measure of the volume of air which enters the apparatus and of the expanded volume which leaves it is easy. The third drying tube which prevents the diffusion of moist air backward was fused, together with a barometer gauge, to a tube leading to an air-tight reservoir of 54.1 litres capacity. When all the drying tubes were in place, the pressure in the reservoir was reduced to such a fraction of an atmosphere that the air passed through the last five bulbs of the six-bulb apparatus at the rate of about two litres an hour. This pressure was observed on the barometer gauge. Call the pressure a . On the next day, or sometimes in twelve hours, the pressure was again observed. Call the second pressure b . The pressure in the reservoir was then again reduced, and the apparatus was ready for another day of action.

Now, disregarding variations of temperature and supposing the barometer constant, remembering that the expansion of the air takes place so slowly that no cooling effect is sensible, we can easily compute the volume of rarefied air which has passed out of the six-bulb apparatus while the pressure has increased from a to b . For this purpose put

w = the weight of the air which would pass through the constriction in the unit of time, if a perfect vacuum were maintained on one side, and the barometric pressure on the other.

x = the pressure in the reservoir.

h = the height of the barometer, assumed constant.

t = the time.

u = the weight of air in the reservoir at the pressure x .

c = the capacity of the reservoir.

l = the weight of a litre of air at the temperature and pressure of the air during the experiment.

V = the volume of rarefied air passing out of the apparatus while the pressure rises from a to b .

The weight of air passing out of the six-bulb apparatus in the unit of time, when the pressure in the vacuum is not zero, but x , may be written $wf(x)$. At normal

pressure, its volume would be $\frac{w}{l} f(x)$, but under the

pressure x , its volume would be $\frac{h}{x} \frac{w}{l} f(x)$, and we there-

fore have $dV = \frac{h}{x} \frac{w}{l} f(x) dt$. Also it is obvious that

$\frac{x}{h} = \frac{u}{cl}$, so that $du = \frac{cl}{h} dx$; and obviously $du = wf(x) dt$.

From the last two equations we find $dt = \frac{cl}{h wf(x)} dx$; and

substituting this value we get $dV = c \frac{dx}{x}$.

Therefore—

$$V = c \int_{x=a}^{x=b} \frac{dx}{x} = c \log \frac{b}{a}.$$

This is the volume of rarefied air which passes the constriction while the pressure rises in the reservoir from a to b . Its volume on entering is computed in an obvious manner.

I have so far made three experiments, as follows:—

	I.	II.	III.
Air entering apparatus = n ..	27 l.	23 l.	58 l.
Mean temperature = t ..	16° C.	15° C.	19° C.
Air leaving apparatus ..	286 l.	228 l.	757 l.
Excess leaving ..	259"	205"	699"
Litres an hour ..	1.6"	1.4"	1.2"
Dilute acid, specific gravity	1.707	1.707	1.566
Vapour tension of water from such acid at temperature t ..	M.m. 0.48	0.43	1.85
M.grms. water taken up by n litres air, at t (computed) ..	M.g. 13	10	106
Specific gravity strong acid at 18°/4° ..	1.8381	1.8381	1.8388
Loss, decimilligrams. ..	5½	4½	18

Experiments 1 and 2 were parts of the same experiment which was interrupted to see if the loss of weight were proportional to the amounts of air in the line marked "excess leaving." In all three experiments, 1163 litres more passed out than entered the apparatus, the sum of the losses in weight is 2.8 milligrams. The amount of sulphur trioxide which escaped may be computed at 0.4 milligram. The remaining 2.4 milligrams. is the weight of aqueous vapour carried out of the apparatus by 1163 litres of air. The quantity subtracted is affected with some uncertainty, since the air used in the experiment on the evaporation of sulphur trioxide was not purified from organic matter, and there may have been reduction of the acid to the dioxide, and reoxidation to sulphuric acid. But with the approximation so far obtained, the water which strong sulphuric acid fails to remove from a slow current of air is about the four hundred and fiftieth or five hundredth part of a milligram. in a litre of air.

Dibbitts* showed that 308 litres of air dried by sulphuric acid gave up 0.7 milligram. to phosphorus pentoxide. It is curious that this is the quantity which my experiments show to be left by sulphuric acid in that quantity of air. The obvious inference may be true, but is not safe. I shall hope to repeat these experiments on the evaporation of sulphur trioxide from sulphuric acid with purified air, and those on residual moisture left in a gas by the acid with some form of apparatus permitting more accurate weighing than Liebig's bulbs.—*American Journal of Science*, No. 176.

Action of Heat upon the Acetones.—MM. Barbier and Roux.—The authors have experimented upon ordinary acetone, benzophenone, and acetophenone. The characteristic action of heat upon these three acetones consists in determining the separation of carbon monoxide and the liberation of the fundamental hydrocarbon groups.—*Comptes Rendus*.

ON THE
ESTIMATION OF ACETIC ACID IN LIQUIDS
CONTAINING ORGANIC MATTER, BY
DISTILLATION.

By H. W. WILEY.

HAVING had occasion to make an examination of some samples of kumys, I was led to enquire whether any other acid except lactic was present. The microscope showed the presence of bacteria aceti, and thus established the presence of acetic acid.

In a substance so complex as kumys the estimation of a minute quantity of acetic acid is a matter of great difficulty. In order to accomplish it in at least an approximate manner I determined to try the method of Duclaux,* which rests upon the assumption that acetic acid in a solution subjected to distillation gives a definite percentage of its weight in given successive portions of the distillate. When ten-elevenths of the original liquid has been distilled the portion of the acid given off amounts to 79.8 per cent.

Mr. A. H. Allen,† who quotes M. Duclaux's results, states that in the only trial he has made of the method, viz., the estimation of the acid in acetate of lime, the quantity obtained was considerably below the amount claimed by M. Duclaux.

This fact caused me to suppose that the actual percentage of acid distilled depended largely on the percentage present, as well as on the total amount of the distillate. In order to submit this idea to the test of experiment I made a large number of distillations of pure fresh milk, to which varying amounts of acetic acid of known strength were added.

I found that in order to have a liquid residue of 10 to 15 c.c. left in the retort when 100 c.c. of milk were used and the distillate equalled 100 c.c. in volume, it was necessary to add to the milk the dilute acid and enough water to bring the total volume up to 130 c.c. After numerous trials I find that at least 15 c.c. of liquid residue should remain in the retort at the end in order to prevent the casein, sugar, &c., from burning.

The quantity of liquid remaining in the retort was determined by pouring the whole of the residue in a linen filter and measuring the volume of the filtrate. In the following experiments the residual liquid varied between 14 and 16 c.c. in quantity. A solution of fifth normal acetic acid was used, of which 1 c.c. contained 0.012 gm. of pure acid.

Since the amount of acetic acid in sour milk or kumys can never be very great in quantity the trials were made with very weak solutions.

The quantities of fifth normal acid used varied from 5 to 30 c.c. in a volume of 130 c.c. A large number of distillations were made in various attempts to prevent the frothing of the acidulated milk and the consequent transfer of portions of it to the distillate. The best methods of preventing frothing will be given hereafter.

METHOD EMPLOYED.

In each case 100 c.c. of milk were used. To this the acetic acid solution was added and then enough water to make the volume up to 130 c.c. Each 10 c.c. of the distillate was titrated separately by N/100 soda, using phenolphthalein as indicator.

Results with 5 c.c. N/5 $\text{HC}_2\text{H}_3\text{O}_2$.

Percentage acid present by weight 0.044. The mean of a large number of distillations showed that the total acid distilled in 100 c.c. when the above amount was present was only 7.33 per cent of the whole. The quantity given off in each 10 c.c. of distillate as well as the total is given below:—

1.	10 c.c. of distillate	0.33 per cent
2.	10	0.33—0.66
3.	10	0.39—1.05
4.	10	0.35—1.40
5.	10	0.40—1.80
6.	10	0.59—2.39
7.	10	0.60—2.99
8.	10	0.90—3.89
9.	10	1.25—5.14
10.	10	2.19—7.33

It may be doubted whether it is worth while to try to estimate so minute a portion of acid as 0.044 per cent, but even this amount can be detected as a trace in a mixture of it with lactic acid, when the latter does not exceed 0.30 per cent, as will be shown subsequently.

Results with 10 c.c. N/5 $\text{HC}_2\text{H}_3\text{O}_2$.

10 c.c. fifth normal acetic acid contain 0.12 gm. anhydrous acid.

In 135 grms. this is 0.089 per cent.

The amount of total acid present coming over with each successive portion of 10 c.c. distillate was as follows (mean of 100 titrations):—

1.	10 c.c.	0.89 per cent
2.	10	1.12—1.91
3.	10	1.27—3.18
4.	10	1.31—4.49
5.	10	1.42—5.91
6.	10	1.59—7.50
7.	10	1.87—9.37
8.	10	2.20—11.57
9.	10	2.69—14.26
10.	10	3.75—18.01

Results with 15 c.c. N/5 $\text{HC}_2\text{H}_3\text{O}_2$.

Following are the mean result of 120 titrations.

Percentage Present.

Fifteen c.c. of fifth normal acetic acid represent a weight of pure acid of 0.18 gm. In 135 grms. of material this represents 0.133 per cent.

The mean percentages of total acid present coming over with each successive 10 c.c. of distillate were as follows:—

1.	10 c.c. of distillate	1.02 per cent
2.	10	1.19—2.21
3.	10	1.28—3.49
4.	10	1.42—4.91
5.	10	1.63—6.54
6.	10	1.97—8.51
7.	10	2.32—10.83
8.	10	2.76—13.59
9.	10	3.44—17.03
10.	10	4.55—21.58

Results with 20 c.c. $\text{HC}_2\text{H}_3\text{O}_2$.

20 c.c. of fifth normal acetic acid have 0.24 gm. of water free acid.

In 135 grms. of material this amounts to 0.178 per cent.

In all 260 titrations were made.

Following are the mean results showing percentage of total acid present, coming over in each successive 10 c.c. of distillate.

1.	10 c.c.	1.30 per cent
2.	10	1.56—2.86
3.	10	1.78—4.64
4.	10	1.88—6.52
5.	10	2.15—8.67
6.	10	2.50—11.17
7.	10	2.90—14.07
8.	10	3.48—17.55
9.	10	4.23—21.78
10.	10	5.58—27.26

* *Ann. d. Chim. et Phys.* (5), xi., p. 233 et seq.

† "Com. Organic Analysis," 2nd edition, i., p. 408 et seq.

Results with 30 c.c. $\text{HC}_2\text{H}_3\text{O}_2$.

30 c.c. N/5 $\text{HC}_2\text{H}_3\text{O}_2$ contain 0.36 grm. anhydrous acid.
In 135 grms. of material this is 0.267 per cent.

The percentage of acid coming over with each successive 10 c.c. distillate was as follows (mean of 120 determinations):—

	10 c.c.	1.80 per cent
1.	10	
2.	10	1.92—3.72
3.	10	2.00—5.72
4.	10	2.13—7.85
5.	10	2.40—10.25
6.	10	2.75—13.00
7.	10	3.03—16.03
8.	10	3.92—19.75
9.	10	4.80—23.95
10.	10	6.13—30.08

It was reasonable to suppose that an organic acid like lactic acid would itself be carried over mechanically to a certain extent in the process of distillation. Since pure acetic acid boils first when the temperature reaches 119° , all that comes over of it also must be carried mechanically in the other vapours or as a definite hydrate of low boiling point. To determine how much of the lactic acid would thus pass over, a large number of trials were made. 20 c.c. N/5 lactic acid in a total weight of 135 grms. were used in these determinations. The amount that came over in each successive portion of 10 c.c. of distillate was almost constant, and did not rapidly increase toward the last, as is always the case with acetic acid. The mean for each 10 c.c. was 0.0064 c.c. of the acid employed, or 0.0016 per cent. For the whole distillate of 100 c.c. this would give 0.016 per cent of the acid present. The percentage of lactic acid in the mixture distilled was 0.27. It is fair to presume that with a larger quantity of lactic acid the amount carried over mechanically must be somewhat greater.

In any case, however, with small percentage of lactic acid, the disturbing effect of the quantity going over can be approximately determined, and in no case is it very great.

It appears therefore that in a total acidity (in kumys or sour milk) of from 0.50 to 1.00 per cent due to the two acids, viz., lactic and acetic, it is possible to determine each of them with a satisfactory degree of accuracy, when the quantity of acetic acid present does not rise above 0.3 or fall below 0.1 per cent. If it should be less than 0.1 per cent the quantities distilled become so minute that the results are not reliable.

It would be interesting to continue the investigations with larger quantities of both acids, but since they do not usually occur in kumys or sour milk in greater amounts, the operations should be conducted in a liquid of a less complex nature than milk.

Separation of the Two Acids in Artificial Mixtures.

To test the accuracy of the determinations I had my assistant, Mr. Dugan, prepare for me various mixtures of milk and the two acids in proportions unknown to me. In most instances I was able to determine with gratifying accuracy the quantities used. In a few cases, however, the results were not accurate, but these were chiefly due to the use of a smaller quantity of the acids than indicated in the limits stated above, for the accuracy of the method.

Following are some of the results of the separation. The quantities of acid employed, as well as of those found by analysis, are given in cubic centimetres of fifth normal acid:—

Trial No. 1.

Found..	..	10.6 c.c. acetic acid.
Given	10.0 „ „
Found..	..	00.0 „ lactic acid.
Given	2.5 „ „

Trial No. 2.

Found..	..	0.92 c.c. acetic acid.
Given	1.00 „ „
Found..	..	8.78 „ lactic acid.
Given	9.00 „ „

Trial No. 3.

Found..	..	0.67 c.c. acetic acid.
Given	0.50 „ „
Found..	..	8.42 „ lactic acid.
Given	9.50 „ „

Trial No. 4.

Found..	..	2.94 c.c. acetic acid.
Given	3.50 „ „
Found..	..	6.29 „ lactic acid.
Given	6.50 „ „

Retention of a Portion of the Acid by the Precipitated Casein.

As I have already mentioned, I find that the best method of clarifying the milk for determining total acid present is by mixing it with an equal volume of strong alcohol. I found, however, using known quantities of acid in the milk, in titrating the filtrate, that the total acidity was not indicated. Here are some of the numbers obtained—in parts of acid known to have been added to the milk:—

1.	94.40 per cent (lactic and acetic).
2.	98.04 „ „ „
3.	86.67 „ (lactic acid alone).
4.	96.20 „ (acetic „ „)

It would appear from the above numbers that lactic acid is held back with more tenacity than acetic. As will be seen, the error which may occur from the above cause is likely to be greater than that arising from the distillation.

The exact cause of the error, its extent, and its remedy are subjects for future study.

As a result of the work the following method of procedure may be recommended:—

1. The sample of sour milk is mixed with an equal volume of alcohol, the acid determined in the filtrate with N/5 NaOH, using phenolphthalein as indicator. The quantity found to be taken at 95 per cent of the amount present.

2. 100 c.c. of the sour milk are diluted to 130 c.c. with water and a distillate of 100 c.c. taken off. The acetic acid in this distillate is estimated (using N/50 or N/100 alkali if necessary).

If less than 12 c.c. N/100 NaOH are required to neutralise the acid in the distillate, it can be assumed that not more than 10 per cent of the acetic acid present has been distilled over. From the total acidity, however, must first be deducted that due to the lactic acid carried over mechanically. If 0.3 per cent lactic acid be present it will be proper to deduct 6 c.c. N/100 from the total used. If 40 c.c. N/100 be required under the conditions above noted, then 18 per cent of the acetic acid may be considered to have come over. If 70 c.c. N/100 NaOH be required the acid distilled over should be estimated at 23 per cent.

If 110 N/100 NaOH be required, place the amount of acid distilled over at 27 per cent.

If the distillate require 200 c.c. N/100 NaOH the quantity of acid distilled over can be taken at 31 per cent.

For quantities intermediate among those given allow for proportionate percentages in the distillate.

Frothing of the Sample during Distillation.

Whether the object of distillation be the estimation of acid or alcohol, the difficulty of preventing frothing of the sample is great. I found that an ordinary test-tube brush, placed in the neck of the flask, was a most excellent

safety plug. The handle of the brush should be cut off so as not to interfere with the stopper. A thread tied to the stump of the handle and left hanging outside does not interfere with the stopper and is convenient for withdrawing the brush. The brush should be at first pushed into the flask, and then, by means of the thread, pulled up into the throat. The bristles then all point downward in a convenient position to puncture the bubbles. For alcohol distillations nothing better than this need be used. In the case of acids, however, there may be some danger of the metal of the brush being attacked, and some other device must be used. I found a small fine sponge pulled into the throat of the flask by a thread very efficient means of arresting the bubbles. Another excellent device is the use of a plug of fine asbestos fibre or of glass-wool. In all these cases the amount of liquid which the plugs will absorb must be approximately known, and this additional quantity of water added to the contents of the flask. I also employed a small platinum cylinder punctured with fine holes, which was attached by a rubber stopper to the delivery tube. The simplest device of all is to use a flask with a side delivery tube. The neck of the flask should be largest at the top and have a small constriction just as it enters the bulb. A perforated platinum cone large enough to fill the neck is placed point down in it. The constriction prevents it from entering the bulb. In this way the bubbles are prevented from entering the delivery tube, and no correction is to be made for absorbed liquids.

CORRESPONDENCE.

RADICAL OR RADICLE?

To the Editor of the Chemical News.

SIR,—Some eighteen years ago, I think, after the word *radical* had long been in use by English chemists, equally with their continental brethren, there was put forth the view that this word was incorrect, and should be replaced by *radicle*. Miller adopted the new word in his last edition of his "Elements of Organic Chemistry" (1869), and the Publication Committee of the Chemical Society has since enforced its use in the *Journal*. The old term has never been seriously defended against the attack then made upon it, yet it is still largely used by eminent chemists in their publications. Recently Mr. Madan, in *Nature*, has attacked the use of *radical* as being incorrect grammatically, and has been replied to in the same journal by Mr. Heyes, who defends the use of *radical* for historical reasons, but apparently admits that *radicle* is the right word, and would have both in use. Here, to me at this date, the matter seems likely to rest, and this I should be sorry to see it do, for I hold not only that *radical* is right, but that *radicle* is wrong—an opinion in which I think there will be many to agree with me.

The word *radical*, we have been told all along by its objectors, is not a *noun*, but an *adjective*, and we are apparently referred to the German for the original use of it in chemistry (Miller, *l.c.*). But the term is much more foreign to German than to English, and both languages owe it, of course, to early French. Besides in German, as in English and French, it is primarily an *adjective*; and why in English it should not be used *substantively* in chemistry, equally as it is in French and German, is to me incomprehensible. Together with the adjective *liberal* it is used in politics as a *noun*, but, for some obscure reason not necessary to fathom, this use of it is held by its opponents in chemistry not to have sufficient analogy. Its use as a *noun* is clearly in accordance with the genius of our language, for we say *animals*, *menials*, *officials*, *principals*, *cardinals*, *fundamentals*, and in Science *proportionals*, *differentials*, *exponentials*, *integrals*, *chemicals*;

why then not *radicals* also? From its earliest use, in French or English, it has meant *pertaining to the essence or principle of things*, and the chemist now uses it for something that he regards as one of the *bases* or *elements* of a substance. *Simple radical* is to him synonymous with *element*, and probably but for the inconsistency of the term *compound element* the word *radical* would not have gained the standing it now has in chemistry. Thus much as to the rightness of the word *radical*.

The word *radicle* is improperly used in chemistry, and should have no place there. It is the *diminutive* of *radix*, and never enjoyed a figurative use until introduced into chemistry. It has always meant *rootlet*, and is still used fully and exclusively in that sense by botanists and anatomists. Those chemists, therefore, who will have *radicle* in place of *radical* can only justify their action by affirming that they regard compound and simple radicals as the *rootlets* of substances. Such a conception is not a happy one, and certainly it is not a true one. Radicals are of the *essence* or *basis*; they are the *elements*, or figuratively the *roots*, of substances. They are all in all to the substance, not some diminutive parts of it. Both Mr. Madan and Mr. Heyes make play upon the words *particle* and *partical*, as though the latter would be analogous to *radical*; but diminutives in *-cle* do not form adjectives in *-cal*, and *radical* gets its *-c-* from *radix* or *radicem*. To use *radicle* for *radical* seems to me as big a blunder as to use *principle* for *principal*, a chief.—I am, &c.,

EDWARD DIVERS.

Tokyo, Japan, June 2, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cii., No. 26, June 28, 1886.

Researches on Ramie.—E. Fremy.—The substances which cement together the fibres and the cellules of this plant are pectose, cutose, and vasculose, all of which can be removed by means of suitable reagents.

Fluorescence Formerly Attributed to Yttria.—Lecoq de Boisbaudran.—(See p. 15).

Action of an Electric Current upon Hydrofluoric Anhydride.—H. Moissan.—On submitting to electrolysis by means of a current of 50 Bunsen elements in a platinum U-tube hydrofluoric acid prepared by M. Frémy's process, and with all the precautions indicated by him, we obtain, on operating at -50° , at the negative pole an escape of hydrogen easily recognised; at the positive pole a continuous current of a gas presenting the following properties:—In presence of mercury it is completely absorbed, with formation of mercury fluoride of a light yellow colour; it decomposes water, giving off ozone; phosphorus is ignited by this gas, yielding phosphorus fluorides; sulphur is heated and melts rapidly; carbon seems to be without action; melted potassium chloride is attacked in the cold with an escape of chlorine; crystalline silicon, washed with nitric and hydrofluoric acids, takes fire in contact with this gas and burns brilliantly, forming silicon fluoride. The electrode of platinum-iridium forming the positive pole is strongly corroded, whilst that of the negative pole is untouched. The most simple explanation of these phenomena is that we are here in presence of fluorine, but it may possibly be a hydrogen perfluoride, or even a mixture of hydrofluoric acid and of ozone active enough to explain the energetic action of this gas upon crystalline silicon.

Spectra of Didymium and Samarium.—Eug. Demarçay.—On examining photographically the ab-

sorption spectra of various products of the fractionation of didymium and samarium the author has obtained some novel results. The fractionations have been partly effected by the method of crystallising the double ammonium nitrates as proposed by Herr Auer von Welsbach, partly by fractionated precipitation with dilute ammonia, but chiefly by a third method. It is known that the spectrum of samarium contains in its violet and ultra-violet portion bands described first by M. de Boisbaudran (*Comptes Rendus*, lxxxix., p. 212) and then by M. Soret (*Archives des Sciences Physiques*, iv., p. 65). Their wave-lengths are:—419—415, 407, 400, 374. The author has observed that the bands 417 and 374 may be very distinctly separated from the band 407 and the band 400, which seem to accompany each other as do the two former bands. Hence samarium, as defined by these four bands, contains in reality at least two simple bodies. If the name samarium is retained for one of them, defined by the bands 407 and 400, the other may be provisionally designated by S_1 . Didymium has been split up by Auer von Welsbach into several bodies:—praseodymium, neodymium, and a third body of which this skilful chemist says nothing, though he has implicitly admitted its existence by eliminating from the spectra of neodymium and praseodymium one of the rays ($\lambda = 476$) of didymium. There is also in didymium a ray ($\lambda = 462$) of which Herr von Welsbach does not speak, and which he does not introduce into his figures, though it is well known. This ray appears to belong to the same body as the ray 471, as they are always found to vary in the same manner. In the spectrum of several fractions there is also a very narrow ray not yet described ($\lambda = 434$ about) which belongs neither to praseodymium nor neodymium. Whether it belongs to the third body ($\lambda = 476$) could not yet be decided. It seems, however, to vary in a rather different manner.

New Double Copper and Ammonium Iodide.—A. Saglier.—This compound is obtained by the direct action of iodine dissolved in alcohol upon the ammoniacal solutions of copper oxide. Its composition is $2NH_3, Cu_3I_2$.

Synthesis of an Inactive Terpinol.—MM. Boucharlat and Lafont.—This compound, obtained by the very prolonged action of glacial acetic acid upon caoutchine is a neutral liquid of a pale amber colour and an aromatic odour. It boils at 110° to 115° in a vacuum and at 220° at the ordinary pressure, but in this case with partial decomposition.

Action of Anhydrous Baryta upon Methylic Alcohol.—M. de Forcrand.—The author has obtained a barium compound, soluble in water and in methylic alcohol.

Decompositions of Pilocarpine.—MM. Hardy and Calmels.—Pilocarpine may be split up by boiling its aqueous solution and by oxidation by means of potassium permanganate.

Zeitschrift für Analytische Chemie.
Vol. xxv., Part 2, 1886.

Separation of Copper from Cadmium.—A. Béhal.—From *Journal de Pharmacie et de Chimie* and already noticed.

Some Characteristic Reactions of the Salts of Gold.—Ad. Carnot.—Noticed under *Comptes Rendus*.

New Method for Determining Chromic Acid in Chromates and Bichromates.—J. W. Chalmers Harvey. From the *CHEMICAL NEWS*.

Determination of Silicon in Iron.—L. Blum.

A New Volumetric Method for Determining Nitrous Acid.—A. G. Green and S. Rideal.—From the *CHEMICAL NEWS*.

Qualitative Detection of Nitric Acid.—A. Arnaud and L. Padé.—From the *Comptes Rendus*.

Determination of Nitrogen Present as Nitric Acid. J. Boyd Kinnear.—From the *CHEMICAL NEWS*.

Method of Obtaining Spark-spectra with Liquids.—E. Demarçay.—Already noticed under *Comptes Rendus*.

Detection of Traces of Nitric Acid.—Curtman (*Pharm. Rundschau* and *Chemiker Zeitung*).—Nitric acid yields with pyrogalllic acid a deep brown mass of so great tinctorial power that by means of this reagent smaller quantities of nitric acid can be detected than with diphenylamine. In this manner one-tenth of a milligramme of nitric acid can be distinguished in a litre of water. The water to be examined is mixed with less than 1 m.grm. pyrogalllic acid per c.c. and 10 to 12 drops of strong sulphuric acid are cautiously let flow into the test-tube, so that two layers are formed. If nitric acid is present the zone of contact turns brown, or, in case of smaller quantities, yellow. P. T. Austen and J. C. Chamberlain (*Amer. Chem. Journal*) recommend, instead of copperas, ferrous-ammonium sulphate for the detection of nitric acid, as it can be kept in solution.

Germanium, a New Non-Metallic Element.—C. Winkler.—Already noticed.

Absorption-Spectra of Various Colouring Matters. Ch. Girard and Pabst.—From the *Comptes Rendus*.

Phenylhydrazine as a Reagent for Aldehydes and Ketones.—E. Fischer.—(*Ber. Deutsch. Chem. Gesellsch.*)

Compounds of Phenylhydrazine with the Sugars.—C. Fischer.—(*Berichte Deutsch. Chem. Gesellsch.*) These two memoirs do not admit of useful abstraction.

The Non-Identity of Arabinose and Lactose.—This subject has been discussed in various journals by Claesson, Kiliani, O'Sullivan, Scheibler, Fischer, and O. von Lippmann.

On Milk-sugar and Galactose.—W. H. Kent and B. Tollens.—From *Tiebig's Annalen*.

On Perseite.—A. Muntz and V. Marcano.—This paper, from the *Annales de Chimie*, is merely mentioned.

Raffinose and Melitose.—This sugar, occurring in beet-treacle and cotton seed, has been the subject of a series of memoirs by Tollens, von Lippmann, Scheibler, Reschbiet, Rithausen, and Böhn.

Nomenclature of the Sugars.—C. Scheibler.—The author proposes that the termination "ose" shall be confined to sugars of the formula $C_6H_{12}O_6$, whilst those of the formula $C_{12}H_{22}O_{11}$ shall terminate in "biose."

Circular Polarisation of Dextrose.—B. Tollens.—The rotatory power decreases with decreasing concentration.

Optical Rotatory Power of Inverted Sugar.—O. Gubbe.—The author examines the influence of the acid used in inversion, the concentration, and the temperature.

The Absorption-Spectra of Alkaloids.—W. N. Hartley.—From the *CHEMICAL NEWS*.

Behaviour of some Alkaloids with Bromine-Water.—C. L. Bloxam.—From the *CHEMICAL NEWS*. The same subject has been further examined by Arnold Eiloart in the same journal.

Characteristic Reactions of Codeine and Æsculine.—L. Raby.—From the *Journal de Pharmacie* and the *Chemiker Zeitung*.

On Officinal Veratrine.—E. Bosetti.—This body is a mixture of two isomeric alkaloids, veratrine (cevadine) and veratridine, the former insoluble in water, the latter soluble.

On Cantharidine.—E. Dietrich.—This compound is characterised by the phenomenon which it displays in the solid state in polarised light, especially when a drop of the solution in chloroform is allowed to evaporate and the residue is examined with the polarising microscope. Its solutions have no effect upon polarised light.

On Kjeldahl's Method for Determining Nitrogen.—G. Czechetka.—Instead of solid permanganate in powder the author uses a saturated solution of this salt in

sulphuric acid, and allows it to flow slowly down into the liquid through a long-necked funnel. He recommends phenolphthaleine instead of litmus.

On Pikrotoxine.—E. Schmidt.—From *Liebig's Annalen*.

Determination of Tannin on Lowenthal's Method.—R. Ulbricht.—The author declares his approval of Schröder's c.c. method. For a standardising substance he recommends potassium quadroxalate, the solution of which, in a sterilised condition, keeps for 14 days. He sterilises also the solution of indigo.

Agreements on the Examination of Articles of Food, &c.—A. Hilger.—The author has published the procedures selected by the Bavarian chemists.

The Fermentive-Power-Tester.—E. Kœlitz.—This instrument, being patented, can be here merely mentioned.

Action of Organic Acids upon Lead and Tin.—F. P. Hall.—From the CHEMICAL NEWS.

Analysis of Copper.—John Pattinson.—From the CHEMICAL NEWS.

Determination of Oxygen in Copper.—O. Pufahl.—(*Berg. u. Hütten Zeitung*).—The author uses 10–20 grms. of bright turnings, not more than 1 m.m. in thickness, carefully removing grease with anhydrous ether. They are weighed in a porcelain boat, and heated for about an hour in a current of pure hydrogen at about 500°. The oxygen is calculated from the loss of weight.

Analysis of Iron.—H. von Jüptner.—(*Chemiker Zeitung*).—Good results are obtained by Drown and Shimer's method for the determination of silica, only if the nitric acid is entirely expelled.

Analysis of Iron and Steel.—F. Watts.—From the CHEMICAL NEWS.

Colorimetric Determination of Carbon in Iron and Steel.—A. E. Hunt.—The author's method is not described.

Determination of Carbon in Iron and Steel.—Sarnstrom.—(*Berg u. Hütten Zeitung*).—The author burns the hydrocarbons, collects the carbonic acid formed in a potash-apparatus, and from its weight determines the carbon volatilised in the form of hydrocarbons.

Determination of Sulphur in Iron and Steel.—G. Craig and H. Rocholl.—From the CHEMICAL NEWS.

The Sulphur in Iron Ores.—V. Eggertz.—(*Berg. u. Hütten Zeitung*). The author points out that barium sulphate, present in many ores, is often overlooked in analyses.

Determination of Phosphorus in Irons.—A. Tamm.—From the *Berg. u. Hütten Zeitung* and the CHEMICAL NEWS.

Distinction between Iron and Steel.—D. Sevoz.—(*Four. Pharm. et Chimie*). Already noticed.

Detection of Slight Gilding and Silvering.—For this paper we must refer to the original.

Specific Gravity of Milk of Lime.—Blattner and G. Lunge.—The author pours the liquid into a hydrometer-glass, inserts the hydrometer and sets the glass in rotation, reading off when the hydrometer ceases sinking.

The Determination of Effective Chlorine in Chloride of Lime.—J. W. Chalmers Harvey.—From the CHEMICAL NEWS.

Testing Petroleum.—Sir F. Abel and Boverton Redwood.—From the CHEMICAL NEWS.

Determination of Free Acid in Tan-Liquors.—B. Kohnstein and F. Simand.—The authors determine volatile organic acids, fixed organic acids, and sulphuric acid.

Detection of Pure Indigo Dye.—Phillips.—(*Chemiker Zeitung*).—The author strips the swatch with warm dilute nitric acid (1 : 6). Cloth dyed with pure indigo takes a straw

colour; that grounded with logwood or sanders takes a more brownish shade.

Testing Saffron-Substitute.—G. Heppe.—This memoir is merely mentioned.

Examination of Vulcanised Caoutchouc.—C. Reinhard.—If incinerated in a muffle the ash is lower than if ignited over a lamp, keeping the temperature so low that the crucible does not become red. The editor cautions against the use of platinum crucibles, as the sample may contain antimony.

Examination of Cinchona Barks.—Squibb.—From the CHEMICAL NEWS.

MISCELLANEOUS.

British Association, Birmingham Meeting, Section B.—It has been arranged that a discussion shall be held at the Birmingham meeting of the British Association, on the Nature of Solution. The discussion will be opened, in Section B, on Friday, Sept. 3rd, by Professor Tilden, F.R.S., and Professor Armstrong, Dr. Gladstone, Professor Guthrie, Professor Hartley, and Dr. W. W. J. Nicol, are expected to take part in it. Gentlemen who are willing to contribute papers on this subject, or to take part in the discussion, are requested to communicate with the president of Section B, Mr. Crookes, F.R.S., at the office of this paper, not later than August 1st.

Celebration of the Centenary of M. Chevreul.—On August 31st M. Chevreul, the *doyen* of the scientists of the entire world, reaches the hundredth year of his life. A subscription has been opened to commemorate this event by a medal, to be executed by M. Roty, and a committee has been formed, under the presidency of M. C. Brongniart. All persons who wish to take part in this tribute of recognition to the illustrious and venerable *savant* may forward their subscriptions to M. Brongniart or to M. Louis Passy, at the offices of the Société d'Agriculture, 18, Rue de Bellechasse, Paris.

MANCHESTER CORPORATION GAS WORKS. T A R.

THE Gas Committee of the Corporation of Manchester are prepared to receive Tenders for the Purchase and Removal of the Tar in stock, and to be produced at their Gaythorn Gas Works during a period of one or more years, commencing from the 1st day of August, 1886. The Committee do not bind themselves to accept the highest or any Tender. Sealed tenders, addressed to the Chairman of the Gas Committee, and endorsed, "Tender for Tar," must be delivered at the Offices of the Gas Department, Town Hall, on or before Wednesday, the 21st of July, 1886.

Forms of Tender and further particulars may be obtained on application in writing to Mr. Charles Nickson, Superintendent of the Department.—By order of the Gas Committee,

JOS. HERON, Town Clerk, Manchester.
Town Hall, 1st July, 1886.

ST. PAUL'S SCHOOL.—An Examination for filling up about 25 Vacancies on the Foundation will be held on the 9th September next.—For information apply to the Bursar, St. Paul's School, West Kensington.

ENAMELLING.

Wanted the address of a Firm or Chemist who will undertake the enamelling of hard soldered German Silver, to stand the action of hot potash and cyanide.—Address for Samples, "Enamel," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

TO MANUFACTURING CHEMISTS.

TO BE LET, a Modern well-built Works, advantageously situated in the immediate neighbourhood of Manchester. Would be adapted to suit any branch, or divided to suit a Tenant at a low rental.—Address, A. B., CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

VOL. LIV. No. 1391.

WHAT IS YTTRIA?

By WILLIAM CROOKES, F.R.S.

A discussion has been going on for some time before the Académie des Sciences between M. Lecoq de Boisbaudran and myself which is likely to turn upon a point in etymology rather than in chemistry.

No longer than twelve months ago the name yttria conveyed a perfectly definite meaning to all chemists. It meant the oxide of the elementary body yttrium. I have in my possession specimens of yttria from M. de Marignac (considered by him to be purer than any chemist had hitherto obtained), from M. Clève (called by him "purissimum"), from M. de Boisbaudran (a sample of which is described by this eminent chemist as "scarcely soiled by traces of other earths"), and also many specimens prepared by myself at different times and purified up to the highest degree known at the time of preparation. Practically these earths are all the same thing, and up to a year ago every living chemist would have described them as identical, *i.e.*, as the oxide of the element yttrium. They are almost indistinguishable one from the other both physically and chemically, and they give my phosphorescent spectra *in vacuo* with such extraordinary brilliancy that it would be absurd to say that the phosphorescence was due to "feeble traces" of impurities.

This is what I formerly called yttria, and have more recently called *old* yttria.

In a subject so obscure as this is it cannot be expected that an ardent worker in his laboratory should always retain perfect consistency in his choice of words; but I must point out, in the use of the word "yttria" as employed by M. de Boisbaudran, a certain ambiguity which is very confusing.

I have never varied in my meaning. By "yttria" I mean now, and always have meant, the yttria of Clève, of Marignac, and of all chemists up to the beginning of this year. I confess, however, I cannot quite make out what precise meaning M. de Boisbaudran attaches to the word yttria. At one time it would seem as if our meanings were identical. Thus, he writes: "It is certain that my earth, very rich in yttria, gives a beautiful spectrum in the vacuum tube." Again, he informs me,—"M. Becquerel has recently examined my earths A and B in ultra-violet light, and has obtained results analogous to yours; that is to say, the earth rich in yttria has generally shone brighter than the other." The earth A, here spoken of, gives my phosphorescent spectrum with wonderful brilliancy, and is the one described above by M. de Boisbaudran as "yttria scarcely soiled by traces of other earths." This yttria, my learned friend goes on to say, is "the same as that of Clève and Marignac, only varying in trifling impurities, Marignac's being perhaps the purest." So far we are agreed in the meaning to be attached to the word yttria.

But M. de Boisbaudran at another time gives the name yttria to an earth of very different properties—to an earth which he has only obtained in most minute quantities after months of unremitting work, to an earth which gives no phosphorescent spectrum in the vacuum tube,—to an earth in fact so difficult to prepare that M. de Boisbaudran himself has not yet succeeded in getting any which really possesses this property. This kind of yttria, therefore, only exists in theory.

What evidence is there that this scanty modicum of ideal earth giving no phosphorescence is really pure yttria? and why may we not call any of the other phosphorescing

earths which M. de Boisbaudran says are impurities, yttria? To refine away the most striking characteristics of a body, to call the *caput mortuum* by the original name, and then dub all the rest *impurities* is an inversion of scientific reasoning which must not be allowed to pass without protest.

It is known to the readers of this Journal that the earth hitherto called yttria is a highly complex molecule, capable with an enormous expenditure of time and material, of being split up into several simpler bodies. Now these constituents of old yttria are not *impurities* in yttria, any more than praseodymium and neodymium (assuming them really to be elementary) would be impurities in didymium. They constitute a veritable splitting-up of the yttrium molecule into its constituents, and when this is done there is nothing left of what used to be called yttria. This being the case I, by right of first discoverer and the general custom obtaining among men of science, am allowed to give these elements any name I like. As, however, some of them might not be new, and it would retard chemical science and bring research into disrepute if new elements were to be rashly thrown into the world with no more justification for their existence than a line in a spectrum, I did not give names to these probationers, but contented myself for the present with calling them $G\alpha$, $G\beta$, $G\gamma$, $G\delta$, $G\epsilon$, $G\zeta$, $G\eta$.

If these really turn out to be new elements, and I decide to call one of them yttrium, I am not exceeding my right to do so; and if I decide that it would introduce confusion to give the same name to a constituent which is already appropriated for the very stable compound molecule in which it occurs, I shall be perfectly within my rights if I give new names to each of the constituents of yttrium. One of the characteristics of what I must call for clearness old yttrium is a well-defined spark spectrum. I have not yet separated the constituents with sufficient accuracy to be able to say which of them gives this spark spectrum. It may be that the particular element to which this is due gives no phosphorescent spectrum; on the other hand the spark spectrum may turn out to be as compound as the original earth, and the well-known lines in it will have to be apportioned between two or more of the new bodies. I wish, however, to emphasise the statements that at present no one constituent of old yttria has any more claim to the paternal name than has any other constituent; that if I like to retain the name yttria for the compound parent molecule and give distinct names to each constituent I may do so; and especially that no one has any right in the present state of the question to call one of the new bodies yttria and to speak of all the others as impurities.

It is well known that M. de Boisbaudran has been working for some time on a new method of spectrum analysis, obtaining *reversion* spectra, by which he has discovered what he considers to be two new earths, $Z\alpha$, $Z\beta$. The details of his method are given in the CHEMICAL NEWS (vol. lii., p. 4), so I need not repeat them. In the hands of a practised experimentalist like M. de Boisbaudran this method may give trustworthy indications, but I must confess that in my opinion the test is one beyond the range of practical analysis, owing to the enormous difficulty of getting the phenomena described by the discoverer. Unless the strength of spark, the concentration and acidity of solution, and the dispersion and magnifying power of the spectroscopic bear a certain ratio one to the other, the observer is likely to fail in seeing a spectrum even in solutions of earths which contain considerable quantities of $Z\alpha$ and $Z\beta$. In my own case I not only have had the advantage of personal instruction in Paris from M. de Boisbaudran himself in the best method of getting these reversion spectra, but on returning to London I brought with me some of the identical earths which give these spectra at their best. In spite of these advantages I have sometimes experimented off and on for weeks without being able to see more than a feeble glimmer of the bands described by M. de Boisbaudran.

Again, when everything is most favourable and the reversion bands are at their strongest, they are but a faint and hazy shadow of the brilliant lines given by the bombardment process. M. de Boisbaudran, speaking of the relative sensitiveness of our two methods, says that the bombardment process *in vacuo* is incomparably more delicate than his reversion test, and I estimate the relative sensitiveness of the two methods to be in the proportion of about 1 to 100.

On reference to my paper in last week's CHEMICAL NEWS (p. 15), it will be seen that I said the earth giving the close pair of greenish blue bands (mean λ 545) was probably gadolinium or $Z\beta$; and on p. 14 I explain this by saying that "gadolinium is composed of at least four simpler bodies," $G\beta$, $G\gamma$, $S\delta$, and $G\zeta$, "the pair of green lines (λ 541 and λ 594, mean 545), being the strongest feature in its spectrum, may be taken as characteristic of gadolinium." In his paper in the same number of the CHEMICAL NEWS M. de Boisbaudran says: "Mr. Crookes appears to attribute to gadolinium the double green band." This is scarcely accurate; I did not ascribe the double green band to gadolinium, but, finding by my test that the so-called gadolinium was a compound body, the earth $G\beta$ being the strongest component, I proposed to attach the name of gadolinium to $G\beta$, rather than give it a new name and so multiply names unnecessarily.

These double green bands are also claimed by M. de Boisbaudran as characteristic of $Z\beta$, and he now admits that his $Z\beta$ is terbia. We have therefore four claimants for the double green bands— $G\beta$, gadolinia, $Z\beta$, and terbia. Until therefore it has been proved that the phosphorescence of the anhydrous sulphates *in vacuo*, and the feeble fluorescence of the hydrochloric solutions by reversion, are caused by the same bodies, I had better adhere to my original suggestion, and speak of the earth as $G\beta$, 545.

I wish to make one thing very clear. I stated before the Royal Society that $G\delta$ was probably M. de Boisbaudran's $Z\alpha$, and that $G\beta$ was probably his $Z\beta$. I do not think my friend has yet proved their identity, but, on the other hand, I cannot say that I am at all certain as to their non-identity. The matter is in a fair way to be settled one way or the other, if my eminent opponent on one side and I myself on the other, each working almost night and day, can settle it. I must, however, state emphatically that I have not the slightest wish to include $Z\alpha$ and $Z\beta$ amongst my new elements. All along I have studiously tried to avoid anything that should seem to favour such a view.

Experimental research is necessarily and slowly progressive, and early provisional hypotheses have to be modified, adjusted, perhaps altogether abandoned, in deference to later observations. We do not censure the dawn for not being full daylight, nor should an experimenter's more advanced researches be used to condemn and discredit his first gropings after truth. We are both working for the truth whithersoever it leads, and, so long as we succeed in finding the truth, I am sure both my learned friend and myself will be content to preserve a philosophic equanimity whether $G\delta$ is really a new earth, whether it is $Z\alpha$, whether $G\beta$ is identical with $Z\beta$, or whether $Z\beta$ proves to be, as M. de Boisbaudran now thinks, terbia.

On the Non-metallic Fluorides.—M. Guntz.—The author has been led by thermo-chemical considerations to think that lead fluoride ought to be decomposed by all the non-metallic chlorides. He, therefore, treated lead fluoride with carbon chloride, sulphur sub-chloride, phosphorus trichloride and oxychloride, obtaining in each case a lead chloride and a fluorine compound. In the case of phosphorus terchloride and oxychloride the gases obtained possess the properties mentioned by M. Moissan.—*Comptes Rendus*, vol. ciii., No. 2.

ON RADIANT MATTER SPECTROSCOPY.*

PART II.—SAMARIUM.

By WILLIAM CROOKES, F.R.S.

(Continued from p. 31).

Is "x" a Mixture?

109. FOR a considerable time strontium minerals and salts only were worked upon, these being considered the cheapest and most fruitful sources of x . A considerable quantity of material was thus accumulated, showing the desired spectrum with great brilliancy. When, however, attempts were made to separate the spectrum-forming body from the accompanying elements, as strontium, calcium, &c., all the foregoing anomalies were displayed. Ultimately two portions of substance were produced—a precipitate (113) containing the supposed new element, and a filtrate, containing the strontium, calcium, and other impurities. Neither the precipitate nor filtrate tested in the usual manner showed the orange band anything like so well as the material before such separation, and indeed at this stage of the experiments it frequently vanished altogether.

Some of the filtrate and precipitate were now mixed together, treated with sulphuric acid, and tested as before: they gave the orange-band spectrum as brightly as did the original substance. The ammonia precipitate was too small for analysis, but judging from its origin it might contain any or all of the rare earths. Chemical analysis showed nothing but a calcium salt in the filtrate.

110. Could it be that the union of two bodies was necessary to give this spectrum, and that calcium was one of these? Could the other constituent be of the nature of an acid such as boric, or a halogen like fluorine?

Many experiments were tried to test this hypothesis. Pure Iceland spar was dissolved in acid, a little of the above described precipitate added, and the mixture tested in the usual way. The orange band appeared again.

Every conceivable mixture was now made of lime with other bodies, but whilst I frequently obtained faint indications of orange band there was never sufficient to satisfy me that I had artificially formed the spectrum-bearing body; the traces observed were evidently due to the all-pervading presence of the sought-for body.

So far all had been contradictory and disheartening. Analogy with the yttrium results failed to throw light to guide through the gloom. The hypothesis that the body sought was an earth, widely diffused in minute quantities only, and that its anhydrous sulphate gave a phosphorescent spectrum in the radiant-matter tube, had guided me a certain distance and then led me widely astray. A new factor must now be taken into account—the presence of a calcium compound appeared to be necessary. An earthy body which, when treated and tested in the usual manner, fails to show the faintest glow of an orange-band spectrum, can by admixture with calcic sulphate be made to yield a pure and brilliant spectrum, rivalling in clearness and beauty that given by yttric sulphate.

111. Of the two components of the phosphorescing body—calcium and x —which is the necessary and which is the variable factor?

This question did not appear difficult to answer. In the first case the calcium must be kept the constant, and x be made the variable quantity.

A piece of pure colourless Iceland spar—the sulphate from which had been proved to phosphoresce normally with a greenish blue light, without bands or concentration in any part of the spectrum (164)—was dissolved in hydrochloric acid, and mixed with about 10 per cent of various metallic sulphates. Sulphuric acid was added, the mixture evaporated to dryness, ignited, and tested in

* A Paper read before the Royal Society, June 18, 1885.

a radiant-matter tube. The bodies thus used to replace x , in addition to the more common earths, were the earths from samarskite—enumerated in the first part of this paper (40)—in as pure a state as I could get them, together with various earthy precipitates, oxalates, &c., obtained from different minerals during the preceding operations.

These experiments resulted in an *embarras de richesse*. Whereas, hitherto, I had considered the orange-band-forming body rare and sparsely distributed, I now found it sharing with yttrium the attribute of ubiquity. The answer to my question was too full, and left me again in doubt as to whether calcium or x was the variable quantity.

The yttrium spectrum turned up in this series of experiments about as frequently as the orange-band spectrum. I knew that in such cases yttrium was present as an impurity; might it not be that the almost universal occurrence of the orange-band spectrum was equally caused by a minute but varying quantity of x in the earths under test?

112. I took them one by one and submitted them to further severe chemical treatment, fractionally precipitating them, in cold dilute solution, with weak ammonia, or fractionally crystallising their oxalates from nitric acid. As the purification progressed the orange-band spectrum generally lessened in intensity till in the case of many earths it faded out altogether, and in most of them it gave evident indications of being extraneous to the earth itself. In some instances, however, the spectrum increased in intensity; moreover, when the purified earth showed any diminution of the orange band the eliminated impurity always showed the orange band in an exalted degree. I drew from these experiments the inference that x was a definite element, as widely distributed, or nearly so, as yttrium, but requiring admixture with a calcium compound to bring out its phosphorescent properties.

113. Next I had to ascertain if the calcium could be replaced by any analogous body. In this case, therefore, the x was kept constant whilst the calcium was replaced. An ammonia precipitate (109) from a rich accumulation of orange-band substance was chosen as the x . Tested in the usual manner, by itself, it showed nothing, but mixed with lime it gave the orange-band spectrum very bright and pure.

The metals used to mix with it were in the form of sulphates—strontium, barium, glucinum, zirconium, thorium, magnesium, zinc, cadmium, lead, copper, silver, cerium, lanthanum, didymium, aluminium, manganese, tin, bismuth, antimony; also silicic, titanitic, tantalic, tungstic, molybdic, and niobic acids. More than half of these bodies possessed the property of conferring "orange-band" phosphorescence on the precipitate under examination, although by themselves they evinced no power of giving a phosphorescent spectrum.

Explanation of foregoing Anomalies.

114. In this manner the remarkable fact was established that the x I sought was an earth which of itself could give little or no phosphorescent spectrum in the radiant-matter tube, but became immediately endowed with this property by admixture with some other substance, which substance likewise by itself had no power of phosphorescing with a discontinuous spectrum.

Of the great number of bodies used to mix with the earth x in these experiments, which acted best? It was not easy to try comparative experiments at this early stage: ultimately I came to the conclusion that lime, if not the best, was as good as any.

115. These results afford a full explanation of the anomalies which had so long hampered my endeavours to repeat on a large scale experiments which, when working with small quantities, had given good results (99, 101, 108). The preliminary experiments were intended to ascertain whether the desired orange band was present or not. Natural impatience led to hurried operations and defective

washing of precipitates, and thus some of the necessary lime was left with the phosphorescing body. The subsequent larger operations were performed in a more systematic manner with the object of securing as large a yield of substance as possible. The precipitates were thoroughly washed, the lime was more completely thrown out, and the sought-for earth, although obtained, refused to reveal itself by the spectroscope and radiant-matter tube.

The contradictory behaviour of the sulphate to water (99) was now easily explained. The insoluble crystals, which from the brilliancy of their phosphorescent spectrum I had at first mistaken for the nearly pure sulphate of x , were merely calcic or strontic sulphate contaminated with perhaps not more than the one ten-thousandth part of x sulphate which it had carried down with them on crystallising.

"X" in Cerite.

116. In the corresponding yttrium research I was aided materially by the fact that the sought-for earth did not give an absorption spectrum (42). This enabled me to throw out a large number of obscurely known elements, and I therefore early endeavoured to ascertain whether the supposed new earth, x , did or did not give an absorption spectrum. At first I could not decide one way or the other. I frequently obtained a good orange-band spectrum when the solutions gave no trace of absorption spectrum, whilst on other occasions the solution showed good didymium and other bands. Gradually, however, it was noticed that whenever the didymium absorption bands were strong the orange-band spectrum was also particularly brilliant. Moreover, amongst the earths enumerated in par. 113 as mixed with lime in the quest for x , I have mentioned that some of them gave the orange-band spectrum with increased intensity; the earths of the cerium group were the most noteworthy, and these considerations made it probable that here would be found the location of x .

117. On a former occasion, when searching for the citron-band-yielding earth, and examining cerite (22 to 25), I made use of the potassic-sulphate method of separating the two great sub-groups, viz., the cerium and the yttrium earths; the former giving insoluble, and the latter soluble, double sulphates. I said (23):—

"The precipitated double sulphates were dissolved in hydrochloric acid, and the earths precipitated as oxalates. After ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and didymia were tested in the radiant-matter tube, but the merest trace only of citron band was visible."

A repetition of the above experiment produced similar results. The contents of the tube were now removed, mixed with lime and excess of sulphuric acid, ignited, and again tested in the tube. This time the orange-band spectrum came out very brilliantly, showing in a striking manner the necessity of supplementing x with some other earth to bring out its phosphorescing properties.

The cerium group, to which x was now almost certainly traced, consists of cerium, lanthanum, didymium, samarium, and perhaps yttrium- α (136). The other metals, enumerated in par. 101 as being precipitated by potassic sulphate, were found not to phosphoresce with a discontinuous spectrum, either alone or when mixed with lime.

Analysis of Cerite.

118. The first necessity was to get the earths ceria, lanthana, and the mixture hitherto called didymia, in a pure state, for my so-called pure earths of this group all showed the orange band in more or less degree.

About 14 lbs. of cerite were finely ground, made into a thick paste with strong sulphuric acid, and heated to drive off excess of acid. The mass became of a white or pale grey colour. This was digested in cold water, filtered, and the residue well washed with cold water.

To the filtrate oxalic acid was added, which precipi-

tated all the earths, with any lime, &c., that might be present as oxalates. It saves times at first only to aim at a partial separation of the mixed earths, and for this purpose it is well to proceed as follows:—The dried oxalates are boiled with strong nitric acid till completely decomposed, the nitrates are evaporated to dryness, mixed with three times their weight of nitre, and fused at the lowest temperature at which nitrous fumes come off; the residue is digested in water, filtered, and washed. The insoluble residue, of a pale yellow colour, consists of ceric oxide and basic ceric nitrate, with a little of the other oxides, whilst the filtrate contains the bulk of the lanthanum, didymium, and samarium.

Separation of Ceria, Lanthana, Didymia, and Samaria.

119. To free the lanthanic, didymic, and samaric nitrates from the last traces of cerium it is necessary to fuse them again very gently with three or four times their weight of potassic nitrate, at a temperature just sufficient to cause slight decomposition. The operation of fusing must be repeated on the evaporated filtrate many times to throw out all the cerium.

The ceric oxide, or basic nitrate obtained, is freed from any didymium by re-treatment with nitric acid and fusion as above; the presence of didymium being indicated by its brown colour or by the absorption spectrum of the solution.

120. The separation from each other of lanthana, didymia, and samaria is a most laborious process, and the amounts of these earths, obtainable in anything like a pure state, is small, compared with the mass of material worked up. The solution of the nitrates of these elements is made perfectly neutral, diluted to such a strength as to contain about 1 per cent of the oxides, and a very dilute solution of ammonia is added, about 0.1 gramme NH_3 in 500 c.c., the precipitation being conducted in large vessels, as ordinary Winchester quart bottles. The first precipitates formed are rich in samarium, and also contain much didymium; these are followed by didymium, with some lanthanum and samarium; and the final precipitates consist almost wholly of lanthanum. By this method there are obtained three portions of hydrates, which must be again worked up separately by precipitation; the first for samarium (113), the second for didymium (127), and the third for lanthanum (125), the process of fractional precipitation being repeated on each portion fifty or a hundred times.

121. The separation of the last traces of didymium from the samarium can be accomplished only by fractional precipitation, an operation so tedious that probably few chemists will be inclined to undertake it. The second portion of hydrates, consisting chiefly of didymium, is purified from the small quantities of samarium and lanthanum by fusing with potassic nitrate, as explained above for the traces of cerium (118); to separate the lanthanum the oxalates are dissolved in warm strong nitric acid, and allowed to cool, when didymic oxalate nearly free from lanthanum is obtained; after repeating several times, the last trace of lanthanum remains in the solution.

122. To separate the small quantity of didymium from the lanthanum obtained in the final precipitates with ammonia, the only method is to continue the process of fractionation; the lanthanic oxide finally obtained should be pure white, any trace of yellow showing that didymium is still present.

123. As cerite contains small quantities of the yttria earths, these must be separated from cerium, didymium, &c., by making a cold solution of the sulphates and adding finely-powdered potassic sulphate in quantity more than sufficient to saturate the solution, allowing the mixture to stand (with frequent agitation) for a few days; filtering, and washing the filtrate with a saturated solution of potassic sulphate. The filtrate contains the yttria earths, and for their complete separation it is advisable to repeat the operation with potassic sulphate three or four times.

The insoluble residues, consisting of a double potassic sulphate with either cerium, didymium, or other member of this group, are boiled with sodic hydrate, filtered, well washed, re-dissolved in nitric acid, precipitated with oxalic acid, and the oxalates ignited, leaving the earths lanthana, didymia, or samaria to be finally purified as described further on.

124. The ceric oxide obtained in the manner just described was white. A considerable thickness of a strong solution did not show a trace of absorption spectrum. The atomic weight of the metal was taken and yielded the number = 141.1

The number given by Böhlig* .. = 141.2

” ” Robinson† .. = 140.2

Many older determinations‡ range from 138 to 139.

This ceric oxide gave no orange-band spectrum in the radiant-matter tube, either with or without the addition of lime.

Purification of Lanthana.

125. The lanthana obtained in the manner described above (120, 122) was more difficult to purify than ceria. Long after the lanthana appeared pure, it gave in the radiant-matter tube a good orange-band spectrum when mixed with lime and treated as usual, although without lime it gave no spectrum.

So long as the lanthana showed the didymium absorption-bands I could not be certain whether the orange-band spectrum belonged to it or to didymium, therefore the tedious process of fractionation with very weak ammonia in cold dilute solutions was repeated for some weeks. The first precipitates were lanthana containing most of the didymia, whilst the final precipitates were lanthana almost if not quite free from didymia, according to the quantity originally present. After several hundred fractional precipitations repeated over and over again, a little lanthana was got which failed to show the didymium absorption-bands. As the purification progressed the phosphorescent orange-band spectrum became fainter, until finally a lanthana was obtained which, mixed with lime and treated in the usual manner, gave no orange-band spectrum whatever. This lanthana was snow-white, and had an atomic weight of 138.3. Marignac gives for lanthana 138.6, Brauner 138.28, Clève 138.22.

Purification of Didymia.

126. The earth formerly called didymia is now known to be a mixture of didymia and samaria. The didymia which I prepared by the method described above, when mixed with lime and sulphuric acid, and tested in the radiant-matter tube, gave the orange-band spectrum as brightly as I had ever seen it. It was not, however, quite free from the accompanying samaria, and systematic operations were now commenced with the object of obtaining the didymia and the samaria in a state of purity,—that is to say, in such a condition that one of them should show no orange-band spectrum at all, whilst the other should give the spectrum in its highest degree of intensity.

I did not attempt the two purifications simultaneously on the same material. One earth only was taken in hand at a time, and by repeated fractionations and the most profuse sacrifice of material I was at last enabled to obtain a little of the desired earth quite free from admixture.

127. I took didymia first. About 1000 grms. of the earth, partially purified as described (120, 121), were dissolved in a large excess of strong nitric acid. To the nearly boiling liquid a hot saturated solution of oxalic acid was carefully added, and constantly stirred, until the precipitate, which at first rapidly disappeared, just refused to dissolve. A drop or two of nitric acid was now added to render the solution clear, and the liquid set aside to

* *Journ. Prakt. Chem.*, (2), xii., 209.

† *CHEMICAL NEWS*, vol. 1., p. 251, Nov. 28, 1884.

‡ *Ibid.*, vol. xlix., p. 282, June 27, 1884.

cool, when brilliant pink-coloured prisms of didymic oxalate (containing nitric acid) crystallised out. These crystals contained nearly all the didymium and samarium, whilst the mother-liquor contained the greater part of the lanthanum—reserved for the preparation of pure lanthana (125).

The crystals of didymic oxalate were ignited and again converted into nitrate, and the above-described partial crystallisation as oxalate repeated five or six times, in each case rejecting the mother-liquor as contaminated with lanthanum.

128. The final oxalates—the ultimate cumulation of the portions least soluble in nitric acid—were next converted into nitrates, and the excess of acid driven off. The anhydrous salt was dissolved in fifty times its weight of water, and fractionally precipitated by ammonia in the following manner:—A large quantity of ammonia was first prepared of the dilution (1 to 5000) used in the previous fractionation (120), and 500 c.c. of this was gradually added, with constant stirring, to Winchester quarts about three-fourths full of the dilute didymic nitrate. In about half an hour another 500 c.c. of ammonia was again added, and this operation was repeated at intervals till the Winchester quarts were full. The bulk of the samaria comes down in the first precipitates, which are filtered off and set aside for the preparation of pure samaria (133).

To the filtrate, containing didymium, with a little samarium and lanthanum, ten successive quantities of about 200 c.c. each of dilute ammonia were added to each Winchester quart at intervals of about an hour, and after violent agitation allowed to subside. The clear supernatant liquid was now poured off, evaporated to about half its bulk, and then, when cold, again poured back into the precipitate, and the operation of precipitating with dilute ammonia was likewise repeated. By this means the greater portion of the samarium present was obtained in the precipitate, whilst the didymium left in solution contained a less proportion of samarium.

129. After a time a balance seemed to be established between the affinities at work, when the earths would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them, when fractionation by ammonia could be again employed.

Samaric nitrate decomposes by heat before didymic nitrate. The nitrates were mixed with four times their weight of potassic nitrate, and the whole kept fused in a crucible till about three-fourths of the earthy nitrates were decomposed. The cooled mass was then dissolved in water, filtered, and the solution evaporated to dryness, and again submitted to fusion. This was repeated several times.

The basic nitrates insoluble in water were dissolved in nitric acid, and put through the operation of fractional precipitation with ammonia, for samaria (133), in the manner just described above (128).

130. To remove the last traces of samarium which might have survived this treatment, the solution of nitrates which had longest resisted decomposition by fusion was now mixed with excess of potassic sulphate. The precipitated double sulphates were subjected to long washing with a saturated solution of potassic sulphate, in which the samarium salt is more soluble than the didymium salt. They were then re-converted into nitrates, and the precipitation and washing with potassic sulphate repeated several times. Finally, the didymium salt was converted into oxalate, and re-crystallised many times from nitric acid, to eliminate any trace of lanthanum that might still contaminate it. Pure didymia is of a very deep chocolate-brown colour.

These proceedings are tedious enough even in their narration, but no mere words can enable the reader to realise the wearisome character of these operations when

repeated day by day, month after month, on long rows of Winchester quart bottles.

131. I commenced the purification of didymia in the latter part of the year 1883, and the operations have been going on since almost daily in my laboratory. At intervals of some weeks the didymia in the then stage of purification was tested in the radiant matter tube, a little lime having previously been added to bring out the discontinuous phosphorescence. During the first month the intensity of the orange-band spectrum scarcely diminished. After this it began to fade, but the last traces of orange band were very stubborn, and not till the last few weeks could I obtain a didymia to show no trace of the orange-band spectrum; and this result has not been accomplished without sacrifice. My 1000 grammes have dwindled away bit by bit, till now less than half a gramme represents all my store.

132. Whilst in the midst of the operations of purifying didymium and samarium I had the pleasure to receive a visit from Prof. Clève, to whom we owe so much of our knowledge of the chemistry of the samarskite and cerite metals, and especially of didymium and samarium. He gave me not only most valuable information, and suggestions respecting the work I was then engaged upon, but on his return to Upsala he munificently presented me with specimens of lanthana, didymia, samaria, yttria, and erbia—specimens at that time considered to represent a state of purity. According to any chemical tests these earths would be deemed absolutely pure, but the test of the phosphorescent spectrum proved too severe a trial, and the didymia, lanthana, and samaria all showed the orange band—the lanthana faintly, the didymia more strongly, and the samaria brightest of all. A subsequent lot of “samarium-free” didymia, sent by Prof. Clève, also gave a strong orange-band spectrum, though the samarium present probably did not amount to more than the one hundred thousandth part of the didymium.

(To be continued.)

LECTURE EXPERIMENT.—THE FERRATES.

By C. L. BLOXAM.

THE ordinary prescriptions for preparing potassium ferrate are not well adapted for lecture illustration. It may be obtained quickly by placing a fragment of potassium hydrate in a little solution of ferric chloride, adding a few drops of bromine, and, if necessary, gently heating; the resulting dark brown mass dissolves in water, yielding a fine red solution which resembles the permanganate in its power of colouring a large volume of water, and may be kept for many hours without decomposition. Barium chloride produces a heavy purplish red precipitate of barium ferrate, leaving the liquid colourless.

A fine red solution of calcium ferrate is obtained by adding a little ferric chloride to bleaching-powder, and boiling with water. This solution also gives a purple precipitate with barium chloride. It is bleached by filtering through paper. It is well known that many samples of bleaching-powder yield a light pink solution when boiled with water, from the production of calcium ferrate; manganous sulphate destroys the pink colour, and barium chloride precipitates the ferrate.

King's College, London.
July 16, 1886.

Detection of Albumen in Urine.—P. Fuerbringer.—The author recommends the capsules prepared by Stütz, of Jena, containing a mixture of the double salt of mercuric chloride and sodium chloride with citric acid. For the same purpose H. Millard recommends a mixture of carbolic acid at 95 per cent, pure acetic acid, and potassa lye in the proportions 2 : 7 : 22.—*Zeitschr. f. Anal. Chem.*

ABSORPTION SPECTRA OF THE ALKALINE CHROMATES AND OF CHROMIC ACID.

By P. SABATIER.

THE author has been for some time conducting researches based on the observation of absorption spectra, which in many cases afford a precise knowledge of the state of dissolved systems and of their progressive modifications. He has given his attention chiefly to chromic acid, the alkaline chromates, and the salts of chromium sesquioxide. His chief object has been to determine the conditions of the transformation of the green salts into the violet or into intermediate conditions.

He employs for these measurements Crova's spectro-photometer. The coloured liquid to be studied is placed in a vertical cylinder of glass, closed at the bottom by a horizontal plate of glass. A cylindrical piston of clear crystal, having the same axis as the cylinder containing the liquid, may be plunged into the latter by means of rack-work. Its position is indicated at any moment by a vernier which is movable along a graduated scale, the zero of which corresponds to the contact of the base of the piston with the flat bottom of the cylinder. This arrangement enables us to intercept between the latter and the transparent piston a liquid column of known height. For this solid piston there has been advantageously substituted a movable hollow cylinder, similar to the external cylinder, having the same axis, but a diameter twice smaller and closed in the same manner by a flat glass at its lower part. We thus can maintain the stratum of liquid traversed by the light constant in thickness, whilst varying its nature, *e.g.*, the outer cylinder receiving a solution of a coloured salt, whilst the inner cylinder contains merely the solvent. The light, directed by reflectors suitably arranged, traverses this apparatus vertically before arriving at the spectro-photometer. The author confines himself at present to indicate the results given by chromic acid and the chromates. The law generally admitted for the transmission of radiation through a thickness e is $I' = Iae^{\alpha}$, α being a fraction which is known as the coefficient of transmission for the ray in question.

For greater convenience he has referred the absorption to solutions which he considers as normal, containing, per litre, 1 eq. or 50.2 grms. of CrO_3 . If the light traverses a thickness of e centimetres of such a solution, we have $I' = Iae^{\alpha}$.

For liquids of different concentrations the absorption will change and will depend, doubtless, merely on the mass of the compound placed in the track of the rays; on condition, however, that the initial equalisation of the two lights has been obtained in presence of one of the same depth of a colourless solvent, which has always been water. If the latter does not introduce any chemical change into the condition of the body we shall have for the energy transmitted $I' = Iae^{\alpha}$, α being the coefficient defined above, e the depth traversed expressed in centimetres, n the number of litres occupied in the actual system by 1 equiv. of chromic acid (50.2 grms.) or by 1 equiv. of the neutral chromate $\text{KCrO}_4 = 97.2$ grms., and 0.5 equiv. of bichromate = 73.7 grms. Thus for the solid crystalline bichromate we have $n = \frac{0.0737}{2.7} = 0.0273$.

The value of α measured for the different wave-lengths with variable thicknesses are sensibly the same, which constitutes a very extensive verification of the law of thickness. For chromic acid the mean values of the coefficients of transmission are—

λ 548	α 0.02
555	0.137
562	0.34
569	0.623
577	0.815
585	0.905
593	0.945

The red ray is transmitted almost unaltered.

The results with potassium and ammonium bichromates are also given in the form of a table. The values found differ very little from those for chromic acid. Hence the absorption exerted by an alkaline bichromate, dissolved or solid, is sensibly identical with that produced by the chromic acid which it contains. With solutions of neutral alkaline chromates the absorption does not reach to the green rays. The absorption exerted by dilute solutions is rather greater, showing a slight dissociation into potassa and bichromate, which exerts an intense extinction upon the radiations in question.—*Comptes Rendus* (vol. ciii., p. 49).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.To COLONEL SIR FRANCIS BOLTON, *Water Examiner*,
Metropolis Water Act, 1871.

London, July 6th, 1886.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, the whole were found to be perfectly clear, bright, and well filtered.

The supply of water to the metropolis during the month of June has maintained the same excellent character which it has manifested now for some months past. Of the 518 samples of water examined during the past three months, no single sample was found to be otherwise than well-filtered, bright, and practically free from colour. The mean amount of organic carbon in the Thames-derived supply for the three months was 0.155 part in 100,000 parts of the water, the mean amount in last month's supply being 0.152 part, and the maximum amount in any one sample being 0.177 part in 100,000 parts of the water.

We have made mention in previous reports of experiments, which have occupied us now for some time past, on the bacteriology of stored and of running water. In the investigation of so extensive and still novel a subject, we have found it necessary to limit ourselves to an attempt at the solution of one or two special points only; and the inquiry, even thus limited, has involved us in a more than anticipated amount of experimental work. Our inquiry is indeed, even yet, far from complete; but certain results have been obtained which seem sufficiently definite to warrant our publication and discussion of them in this and succeeding monthly reports.

Leaving to others the mere determination of the relative numbers of innocuous and presumably beneficent forms of microbe life present in different examples of water-supply, we have attempted to find out something

in respect to the conditions necessary for the continued existence, development, and propagation in water, otherwise wholesome, of extraneous morbid forms purposely introduced therein, with a view to learn how far such introduced forms thrive and increase, or dwindle and die out in their environment of wholesome water, and how large or otherwise is the extent of pollution to which water must be subjected in order to allow of the introduced morbid microbes sustaining their existence therein for more than a few hours. Taking advantage of the experience common to all workers in bacteriology, as to the advisability of simplifying the experimental conditions as much as possible, and as to the paramount necessity of dealing with some or other isolated form of microbe apart from all other forms, our investigations have been conducted almost exclusively with the particular micro-organism characteristic of splenic fever, and known as *bacillus anthracis*. The mode of experimenting we have usually resorted to is as follows:—Different sorts of wholesome water were infected with a greater or less proportion of proteid liquid laden with this particular bacillus. The so-infected water having been kept at varied known temperatures for a greater or less number of hours, portions of it were added to sterilised culture-fluid or culture-jelly, and observation was made as to whether or not there occurred in the culture medium a consequent growth of bacillus. The general result was as follows:—Water which had been infected within a few hours only was found to possess the property of setting up a characteristic growth of bacillus in the culture medium to which it was added, whereas the same infected water, after it had been kept for some time longer, was found to have lost altogether this particular property. Or to state the result in another way, the existence of *bacillus anthracis* in water purposely infected with the bacillus, though abundantly evident within a few hours of the infection, was not recognisable after a longer interval. Details of some of the series of experiments made respectively with sterilised distilled water, with sterilised and decarbonated town-supply water, with sterilised but not decarbonated town-supply water, with non-sterilised town-supply water, and with non-sterilised running stream water, will be given in our future monthly reports.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

THE PURIFICATION OF WATER BY ALUM.

By Prof. PETER T. AUSTEN, Ph.D., F.C.S.

THERE is no subject which gives the manufacturer greater anxiety at times than the water which he is using in the works. Even where he is so lucky as to be located on the banks of some clear and sparkling brook, and hence is free from many of the troubles known to his less fortunate brethren, his brook may not seldom get into a troubled state and refuse to be clarified of its suspended clay and other matters by an ordinary process available to him. In no industry is this vexation from dirty water greater than in dyeing. Hence it is a matter of great importance, meaning a saving of hundreds and sometimes thousands of dollars, to have a simple means of clearing water, so that it can be used in ordinary manufacturing processes, and yet not in any way injure the properties of the water for subsequent use.

For large works which use water requiring continual purification, some constant process should be employed, as the Hyatt filter, for instance. The Norfolk and New Brunswick Hosieries filter all the water which they use in their works, and in this way get a most beautifully clear and sparkling water out of a rather muddy looking source

(the canal). In this establishment four large Hyatt filters are used, and I have had occasion to satisfy myself of the efficacy of their working. But there are many small establishments which could not afford to put in large filters and pumps, and there are many others which do not require to purify their water, except at certain seasons of the year. Hence some simple process is needed, one that can be worked without trouble and which will give a clear water, and by which no detrimental qualities shall be added to the water.

In a recent report to the State Geologist of New Jersey on the purification of drinking water by alum, I have, in conjunction with Prof. F. A. Wilber, made this matter of the clarification of water the subject of a special investigation. The use of alum as a purifier of water seems to date back a long time. Particular attention was directed to its use by Jeunet in 1865, in an article published in the *Moniteur Scientifique*. He found that 0.4 grm. of alum to a litre of water (23.3 grains to a gallon) rendered it drinkable, even when it was quite full of foreign matter. The time taken for this clarification was from seven to seventeen minutes.

Alum is a double sulphate of potassium and aluminum, and in this case breaks into potassium sulphate, which remains in solution, and a basic aluminic sulphate. This basic aluminic sulphate, the composition of which is undetermined, precipitates as a more or less gelatinous and flocculent mass, and carries down with it the foreign matters and humus bodies. The sulphuric acid set free in the formation of the basic aluminic sulphate attacks the earthy and alkaline carbonates which are always present, and forms with them sulphates, setting the carbonic acid free. Aluminic sulphate acts like alum. Ferric chloride (perchloride of iron) acts in the same way as alum.

In late years an extensive use has been made of alum in the many processes of purifying water, sewage, &c. It is not improbable that, aside from its effect in precipitating matter mechanically by envelopment within the precipitating basic aluminic sulphate, the alum exerts a distinct coagulative action on the albuminous substances in the water, rendering them insoluble, and thus causing their precipitation; perhaps the same or similar effect that alum produces in the tawing of leather. Alum has the great advantage that it is cheap, can be obtained everywhere, and is not highly poisonous. Thirty grains can be given at a dose, and the dose repeated four times a day without danger. Then again it has another very great argument in its favour, and that is its cheapness. To get practical results from the purification by alum it is evident that it must be added in very small amounts. The amount of alum used by Jeunet seemed to be unnecessarily high. On repeating his experiments, using New Brunswick hydrant water, which at the time the experiments were made carried considerable clayey matter, we found 23.3 grains of alum to a gallon produced an immediate coagulation of the suspended matters in the water, but no settling took place under six hours or more, as stated by Jeunet. On longer standing, however, the water settled perfectly, and was as clear as could be wished for. The water after treatment had no taste of alum, but gave a perceptible test for alumina, showing that some alum remained in solution. Our next procedure was to determine what was the minimum amount of alum that was needed to clarify this particular water. Tall cylinders were filled with water and alum added in varying amounts. Depending on the amounts of alum added, gelatinous precipitates settled out after a greater or lesser lapse of time. It would be impossible to make any general rule for the addition of alum to water, because the amount of impurities will of course be very much greater in one sample of water than in another, but we were able to determine what the practical minimum limits were for this particular water. 1.2 grains of alum to the gallon was about as small an amount of alum as it seemed practical to use to get a perfect separation of the impurities. The larger the amount of alum added to the water, the more

quickly will the separation take place; the smaller the amount added, the longer will the water have to stand before a clarification will be effected. Again, large bodies of water will be precipitated by smaller amounts of alum than one would infer from experiments on a small scale, as the mechanical action of the precipitate here, in enveloping and carrying down suspended matter, is greater in a large body of water than in a small one. It will be better, however, to err on the side of too large an amount, for even then the amount of alum added will be insufficient to impart any detrimental properties to the water.

Sixteen galls. of the city water were treated with 31 grs. of alum and the whole allowed to stand. After 48 hours the precipitation seemed complete and the bottom of the vessel was covered with a brownish slimy deposit. This substance after being dried gave 59.28 per cent of ash which contained silica and alumina in relatively large amounts. The clear water gave no reaction for alumina, showing that there was no free alum in solution. The addition of more alum to the water failed to produce any further precipitation, showing that all the matter precipitable by alum had been thrown down.

It may hence be inferred that the addition of 2 grains of alum to a gallon of water will clarify it by standing. Some waters may require less, and some may require a longer standing than 48 hours, but this is a matter very easily determined for any particular case which may arise.

The water, after precipitation has taken place, is perfectly clear and sparkling, and has neither taste nor smell imparted to it. For use in the dye house there can be no possible objection made to it. The most practical way of applying this method in clarifying water for use in manufacturing where filters are not used, will be as follows. Two vats, or hogsheads, or similar deep tanks, are filled with the water and treated with alum at the rate of half an ounce of alum for every 100 gallons of water. The alum should be dissolved in a little hot water, so that it can be mixed with the large bulk of water without difficulty. The mixing can be done with a long handled dyer's stirrer. A few minutes' stirring will suffice to mix the alum and the water very thoroughly. After the mixing has been done, the water should be allowed to stand undisturbed for 48 hours or until the water clarifies, which can be easily seen by its appearance. If the clarification takes place in less time, so much the better. The water is now racked off for use. When the vat has been emptied to as low a level as is possible without disturbing the sediment, the plug in the bottom should be knocked out and the vat cleaned out with a strong jet of water. The slimy deposit is easily dislodged and washed away by a stream of water. While one reservoir is thus being used the other is full of water precipitating, so that the supply is continuous. The best means of drawing the water from the tanks without disturbing the sediment is about as follows:—The pipe should enter the side of the vat and pass to the middle and there be bent upwards so as to end about a foot above the bottom of the vat. The water is thus drawn downward, and no agitating of the bottom is produced. If the pipe is turned toward the bottom of the vat, the current of water will disturb the sediment.

I think that this method will be found of very great value to many works which now have trouble with their water in the rainy season, and I can call to mind offhand several which could use it to advantage. A few trials with the beautifully clear water produced by the alum treatment will make the hands feel loth to go back to the natural water even at its best. I am quite certain that many streams not now available to the manufacturer can be made so by this treatment.—*Textile Colorist*.

The Action of Aniline upon Orcine.—A. Zega and K. Buch.—In contact with aniline orcin loses its hydroxyl groups successively, and becoming first an oxyamine and then a diamine.—*Journ. f. Prakt. Chemie*.

NOTICES OF BOOKS.

Chemistry of the Carbon Compounds, or Organic Chemistry. By Prof. VICTOR VON RICHTER. Authorised Translation, by EDGAR F. SMITH, Professor of Chemistry, Wittenberg College, Springfield, Ohio. From the Fourth German Edition. London: H. Kimpton.

THIS book, if we may judge from the peculiarities of the orthography, has evidently been printed on the other side of the Atlantic. The language and terminology employed are also peculiar. We find the illogical term "metalloids" applied to the non-metallic elements. "Magenta" is not mentioned either in the text or in the index, the author having preferred to retain the Franco-German name "fuchsine"—unpronounceable by every Englishman who is not a German scholar. Cerulignone is here called "cœroulignone." *Carthamus tinctorius* is another peculiarity; the plant is commonly known as *Carthamus tinctorius*. Extract of indigo is spoken of as indigo-carmine, and in the same paragraph we read—"Or the indigo-blue is changed by fermentation to indigo-white, the weaving saturated with the latter, &c." Now "the weaving" is certainly a literal version of the German original "das Gewebe," but the idiomatic and intelligible English rendering would be "the tissue." In the section on Uric Acid we find the unusual terms "Carnivoræ" and "Herbivoræ." In short, the reader will occasionally feel tempted to remark that Prof. von Richter's work might well have claimed a more careful translation.

The author's object has evidently been to produce a text-book holding a somewhat intermediate rank between those sketchy manuals with which we are but too familiar and such works as those of Professors Roscoe and Schorlemmer. As far as was possible within the compass of 694 pages he has been fairly successful. The index might have been advantageously rendered more complete.

First Lessons in Practical Chemistry: an Introduction to the Study of Qualitative Analysis. By A. HUMBOLDT SEXTON, F.C.S., Professor of Chemistry in the College of Science and Arts, Glasgow. Glasgow: Hadden.

WE have here a pamphlet of 32 pages. The author complains that the course of practical laboratory work usually followed has been subjected to several attacks and denounced as "test-tubing." He admits that it is "open to grave objections, one of the most important being that it is often quite impossible to say how far the results entered in the laboratory-book have been actually observed, or how far they have been copied from the text-book." He has therefore drawn up his exercises in such a manner as to ensure, as far as possible, that the student may actually observe the facts which he records. He expresses strong doubts as to the expediency of putting even simple quantitative experiments into the hands of beginners.

The teachings of the book are divided into twenty-five lessons, followed by instructions on the preparation of reagents. Here we perceive that whilst the possible impurities of sulphuric acid are noticed, those which may occur in hydrochloric and nitric acids are overlooked, and that ammonia is altogether omitted.

The Retrospect of Medicine. A Half-yearly Journal, containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by JAMES BRAITHWAITE, M.D. Lond. Vol. xciii. Jan. to June, 1886. London: Simpkin, Marshall, and Co.

THIS volume contains little which can legitimately claim our notice. Lead poisoning seems to be attracting considerable attention. None of the cases here referred to, however, seem traceable to the use of water which has

traversed lead pipes or has stood in lead cisterns. Cocaine, now so fashionable, seems to possess well-marked poisonous properties, though no fatal case is recorded.

Annual Report of the Board of Regents of the Smithsonian Institution: showing the Operations, Expenditures, and Condition of the Institution for the Year 1884. Washington: Government Printing-Office. 1885.

THIS volume contains some curious facts concerning Smithson, the founder of the Institution. His name appears to have been Macie, but he assumed, by Royal license, the name of his putative father, Smithson, curiously designated the *first* Duke of Northumberland.

The energy with which Americans are carrying on scientific exploration in all parts of the world is highly deserving of honour, the more as it is not a mask for covering military and political intrigues. We notice here the proposal made by Prof. V. Ball, of the University of Dublin, that an Institution like the Smithsonian would be very useful in England.

The "Record of Scientific Progress" is an important and elaborate feature, but the facts laid down are of course by this time generally known. Of this report 174 pages are devoted to meteorology, whilst physics claims only 56 and chemistry 51.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors, 1886. Gresham College, E.C.

AMONG the efforts now being made to place technical training in England in a position commensurate with the necessities of our national position, the establishment and maintenance of the City and Guilds of London Institute occupies a position of increasing importance. The Report before us expresses the hope that "the advantages offered by the Central Institution will enable parents to secure in England for their sons Technical Instruction of the same high class as has been for so many years provided in the great Technical Colleges on the Continent: it is hoped that students trained in the Central Institution will gradually occupy the places in manufacturing works, and especially in Chemical works, both in England and the Colonies, which now for some years have been almost monopolised by the Germans and the Swiss."

That such may be the case we most devoutly trust; but to ensure the success, in its highest sense, of the Institution something more than a sufficiency of funds will be requisite. Two evils in the character of the teachings given will have to be avoided. One of these is the teaching of processes to the exclusion of principles, forgetting that processes may be improved upon or superseded, whilst principles are always applicable. The other danger is one peculiarly English; it consists in teaching the student to talk about things rather than to do them. This is an inevitable consequence of the exaggerated importance which in these realms—and nowhere else save in China—is attached to examinations. What is wanted is that, as was well said by Prof. H. E. Armstrong last year in his Presidential Address to the Chemical Section of the British Association, "an atmosphere of research must pervade the College." Whatever stands in the way of this end must be sacrificed without scruple.

Prix Courant Général des Produits Chimiques et Pharmaceutiques. Paris: Billault, 22, Rue de la Sorbonne.

THIS establishment, the successor to the firm of Billault and Billandot, as well as to Robiquet and the Pelletiers, issues a very complete price list of drugs and chemicals. We find here aluminium carbonate—a substance lately patented in this country as a precipitant for sewage—offered at 3 francs per kilo. Vanadium still maintains its

rank as the costliest product which comes into the hands of the chemist; it is quoted at 70 frs. per grm., or more than seventeen times the price of chemically pure gold. Metallic cerium figures at 40 frs. per grm. A curious product, which we have never met with before in any price-current, is chitine, obtained from coleopterous insects. Phenol-phthaleine, which is strangely absent in some catalogues which have reached us, is quoted at the very reasonable figure of 20 centimes per grm.

The least satisfactory point in this list is that salts are classified under their constituent acids, and are thus often inconveniently removed from their bases.

CORRESPONDENCE.

PROF. DITTMAR'S "ANALYTICAL CHEMISTRY."

To the Editor of the Chemical News.

SIR,—In looking over the notice of this useful little book in your issue for the 9th inst. (CHEM. NEWS, vol. liv., p. 21), I saw with equal surprise and regret that I have described the first part as being substantially unaltered whilst the appendix had been re-written; the reverse is to a great extent the case.—I am, &c.,

YOUR REVIEWER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 1, July 5, 1886.

Electro-Conductivity of Mixtures of Neutral Salts. E. Bouty.—The author notes that no general rule enables us to deduce exactly the conductivity of mixtures of neutral salts from that of simple saline solutions. He inclines to the opinion that the difficulty of the problem depends not on the nature of electro-conductivity itself, but on the variability of the chemical equilibria possible in solutions.

Decomposition of Ferric Chloride by Water.—G. Foussereau.—In the decomposition of this salt by water two very distinct reactions may be produced. On the one hand the acid and the base separate, giving rise, by a reversible phenomenon, to soluble hydrated products, the formation of which is shown by a reddish colouration of the liquid. On the other hand, a portion of the oxide or of the oxychloride separated may undergo a molecular modification and be precipitated as an insoluble oxide. This latter effect is not reversible and does not occur in very dilute liquids.

Absorption-Spectra of the Alkaline Chromates and of Chromic Acid.—P. Sabatier.—(See p. 44).

Transformation-Heat of Vitreous Selenium into Metallic Selenium.—Ch. Fabre.—The mean quantity of heat liberated in the change of state of selenium is +2.88 calories.

Action of Vanadic Acid upon the Alkaline Haloid Salts.—A. Ditte.—The author has studied the behaviour of vanadic acid with potassium iodide, bromide, chloride, and cyanide. With the haloid salts of sodium and ammonium the reactions are quite similar, but the fluorides form an exception.

On Barium Hydrate.—M. de Forcrand.—The author has previously obtained and described two crystalline compounds obtained on dissolving anhydrous barium

oxide. He now finds that these crystals, if heated at 135° in a current of dry hydrogen, lose 31.85 per cent of their weight, and leave normal barium hydroxide still contaminated with 3 to 4 per cent of methylic alcohol.

Contribution to the Study of the Alkaloids.—Oechsner de Coninck.—Synthetic quinoleine iodo-methylate and pyridin iodomethylate are mixed in equimolecular proportions. The mixture is dissolved in hot absolute alcohol, adding an excess of potash lye at 45° , when the liquid turns from bright red to reddish brown. It is heated in the water-bath for an hour, when a brownish resin is formed. The liquor is decanted into another flask, a little potassa is added, and heat is applied for an hour longer. The resin is allowed to drain and is then dissolved separately in methylic, ethylic, and amylic alcohols and in ether. The solutions thus obtained are all reddish brown by reflected, but a fine ruby-red by transmitted light. The next day there is found in the second flask a viscous mass, which is exhausted with hot absolute alcohol and filtered through fine paper. The filtrate is of a garnet-red. Its reactions distinguish the colours described in the author's last memoir from those now described. He has prepared in the same manner the derivative colours from various isomeric mixtures. The colours vary not merely with the nature of the alcoholic radicle combined, but with the position which it occupies in the compound. He has examined, also, the iodomethylates of dipyridin, α -dipicoline, β -dipicoline, β -dilutidine, and γ -dilutidine.

Isomerism of the Camphols and Camphors.—Alb. Haller.—The author tabulates the camphols of N'gai, of mother-wort, and Bang-phien, each with its corresponding camphor, monobromo-camphor, and camphoric acid, showing their respective fusion-points and rotatory powers.

Researches on the Composition of the Suint of Sheep's Wool.—A. Buisine.—The author refers to the complex nature of suint, consisting of two distinct portions, the sudoric and the sebaceous secretions. The former portion is soluble in pure water, whilst the latter is removed from the wool only by means of soap-lyes, &c. The sudoric liquid of the sheep holds in solution free carbonic acid; ammonium and potassium carbonates; fatty volatile acids, the acetic, propionic, butyric, valerianic, and caproic; fatty acids higher in the series, especially the oenanthylic and capric; oleic and stearic acids and certain waxy acids, among which is the cerotic. These acids exist in the suint-washings in the state of potash soaps. There is further suint-grease in the state of emulsion, phenol as potassium phenylsulphate, sarcosolactic, benzoic, oxalic, succinic, and uric acids; amidic acids, glycocoll, leucine, and tyrosine, and colouring-matters analogous to those of urine.

Acidimetric Determination of Sulphurous Acid.—Ch. Blarez.—From the author's experiments it appears that sulphurous acid does not behave in the same manner with the various alkalimetric indicators. With phenolphthalein it possesses a basicity twice as great as with cochineal, helianthine, and acid magenta. The last-mentioned indicator indicates only the partial neutralisation of sulphurous acid when the neutralisation of the first half has been slightly exceeded. Litmus, Poirrier's blue C₄B, as well as baryta-water and ammonia, do not give distinct results.

Acidimetric Determination of the Apparent Acidity and Acidimetric Determination of the Sulphurous Acid.—Each c.c. of the decinormal alkaline liquid represents 0.0032 grm. of SO₂ if we use phenolphthalein or 0.0064 grm. SO₂ if we employ cochineal or helianthine. The following are the results of direct determinations, giving the quantity of SO₂ in weight per litre:—Titration with iodine, 3.840 grms.; with phenolphthaleine, 3.776 grms.; with cochineal, 3.792; and with helianthine, 3.795. Hence the acidimetric determination of sulphurous acid is sufficiently exact whenever possible. The acidimetric determination of free sulphurous acid in presence

of other free acids is practicable only in case of a mono or polybasic acid so strong that its absolute basicity can be shown by cochineal or helianthine. In this case we make two successive determinations, one with cochineal or helianthine and the other with phenolphthalein. The difference expressed in c.c. of decinormal alkali multiplied by 0.0064 gives the weight of sulphurous anhydride in the volume of the solution operated upon. This method has been verified in presence of nitric acid (added at the very moment of titration) hydrochloric, sulphuric, and oxalic acids. The results were in every case satisfactory. This method is applicable also in the titration of sulphites and in the study of their aqueous solutions. The acid sulphites with an excess of sulphurous acid appear acid to cochineal and helianthine. With these reagents and a standard alkali their excess of sulphurous acid may be determined. The acid sulphites are neutral to cochineal and helianthine; if mixed with phenolphthalein they appear acid, and they absorb, before showing the rose colouration which this reagent takes in contact with bases, as much alkali as they already contain. The neutral sulphites, alkaline with respect to cochineal and helianthine and neutral to phenolphthalein, are brought to the state of acid sulphites by an addition of sulphurous acid equal to that which they already contain. It is preferable, however, to employ decinormal hydrochloric acid. A slight excess of this liquid is added, making use of cochineal or helianthine, and it is brought back to the turning-point with decinormal alkali. If we have an intermediate sulphite containing, for 1 mol. of sulphurous acid more than 1 but less than 2 mols. of alkali, we may find its exact composition by means of the two following determinations:—*a*, to a given volume of the solution is added standard alkali until the phenolphthalein changes colour; *b*, to a similar volume of the same solution is added an excess of decinormal hydrochloric acid so as to pass the turning-point of cochineal or of helianthine, and the excess is determined by the addition of decinormal alkali. The sum obtained by the addition of the volume of alkali used in *a* and of the volume of acid really utilised in *b*, calculated as sulphurous acid, shows the quantity of this body contained in the volume of liquid operated on. Now, as we know the weight of sulphurous acid contained in a given volume of liquid and the weight of alkali necessary to transform it into a neutral sulphite (experiment *a*) we find by difference the weight of combined alkali and consequently the exact composition of the compound.

Development of the Sugar-Beet; Study of the Leaves.—Aimé Girard.—Not susceptible of useful abstraction.

Justus Liebig's Annalen der Chemie,
Vol. ccxxxiii., Part 2.

On the Uranium Compounds.—G. Alibegoff.

Separation of Uranium from the Alkaline Earths and Alkalies and its Determination.—G. Alibegoff.—In the second of these memoirs the author shows that neither ammonium sulphide, nor ammonium carbonate followed by ammonium oxalate, as proposed by Foulon, can be successfully used for separating uranium from calcium. He recommends mercury oxide with the addition of ammonium or sodium chloride. The precipitate is washed with a very dilute solution of ammonium chloride. For the determination of uranium a measured quantity of solution of uranyl chloride is mixed with a few drops of ammonium chloride in a beaker and heated to a boil; pure elutriated mercury oxide is then added, carefully avoiding excess. The liquid is then brought again to a boil, shaking occasionally. Stirring with a glass rod is not recommended, as the precipitate attaches itself firmly to parts of the beaker which have been rubbed with the rod. The beaker is let stand in cold water until cold. The clear supernatant liquid is then repeatedly decanted off, the precipitate is brought upon the filter and washed with

water containing ammonium chloride. All this must be done in the cold. The use of the filter-pump cannot be recommended. The washed precipitate, together with the filter, are placed in a platinum crucible and heated, at first cautiously, then gradually to ignition, the lid being removed, and finally converted by the blast-lamp into olive-green uranoso-uranic oxide, in which form it is weighed. In the separation of uranium from calcium and strontium, a small quantity of the latter may be carried down, if they are present in excess, but they may easily be removed by boiling up the precipitate after decantation a couple of times with water containing sal-ammoniac, and filtering when cold. The slightest trace of the alkaline earths in the precipitate may be recognised by the presence of yellow or orange-coloured particles in the olive-green mass after ignition. The separation of barium from uranium is preferably effected by means of sulphuric acid. To mixtures of the chlorides of uranium and magnesium there is added first a sufficiency of ammonium chloride, and the mixture is boiled up. On the subsequent addition of mercury oxide uranium is deposited alone. If alkaline earths occur along with alkalies and uranium mercury oxide may be used with success.

Communications from the Laboratory of the University of Graz.—These include a memoir by Alfred Popper on the Atomic Weight of Antimony. The author in his latest and most careful determinations obtains a mean value of 120.69, or an entire unit more than J. P. Cooke's result, 119.60. He can find no source of error either in Cooke's determinations or in his own, and suggests that the possible presence of germanium may solve the question. From the same laboratory we have an account of nickel-carbide, by L. Pebal, and a note by Fr. Iwig and O. Hecht on the calcium salts of malic acid.

Communication from the Main Chemical Laboratory of the University of Tübingen.—This consists of an investigation by A. Römer on the influence of volumes upon the chloration of combustible gases.

Communications from the Chemical Laboratory of the University of Geneva.—These include a paper by A. Rée on β -sulphophthalic acid, β -oxyphthalic acid, and β -chlorophthalic acid, and a memoir by C. Graebe and Ph. Guye on the formation of diphtalyl.

Zeitschrift für Analytische Chemie.
Vol. xxv., Part 2, 1886.

Examination of Mixed Tissues and Yarns.—A. Gawalowski.—The author determines actual solids on 2.5 grms. by drying at 100° in a special apparatus. The fat is obtained by extracting 15–20 grms. of the sample, gently dried, with the purest petroleum ether, evaporating and weighing the residual fat. Soaps, resin, alkali, pigments, &c., are obtained by extracting the sample freed from fat, first with boiling water and then with a mixture of 2 parts absolute alcohol and 1 part ethylic ether. The residue is dried at 100° and weighed. To determine wool this residue is steeped for 12 hours in a cold acid containing 60 per cent. of sulphuric anhydride, carefully transferred to three times the volume of cold water, filtered, perfectly washed with hot water and weighed as wool. The difference is cotton, linen, hemp, or silk waste.

Examination of Manures and Soils.—H. H. B. Shepherd, P. de Gasparin, G. Lechartier, A. Carnot, &c.—From the CHEMICAL NEWS, *Comptes Rendus*, and other publications.

Separation of Chlorophyll.—Tschirch.—(*Chemiker Zeitung*). This may be effected by precipitating the green alcoholic solution with solution of barium hydroxide.

Solubility of Calcium Phosphate in Urine.—A. Ott.—Neutral calcium phosphate requires the presence of salts, which increase its solubility, to explain the proportion in which it is found in urine.

Titration of Urea with Bromine Lye (Hanburger's Method).—E. Pflüger and F. Schenck.—The process does not give satisfactory results.

Determination of Nitrogen and Chlorides in the Urine of Dogs.—As regards nitrogen Kjeldahl's method gives comparable results. The determinations of the chlorides made according to Habel, Fernholz, Arnold and Mering are also concordant.

On the Multiplier in Determining Sugar in Urine.—Worm-Müller.—The multiplier 230 is found sufficiently accurate for urines containing more than 0.5 per cent of sugar.

On Mucus-Matters.—O. Hammarsten.—The mucine of snails is a mixture of true mucine and mucoid matters.

A Method for Determining the Relative Proportions of Pepsine.—E. Schutz.—This memoir does not admit of useful abstraction.

The Acrid and Volatile Constituents of certain Ranunculaceæ.—H. Beckurts.—(*Chemiker Zeitung*). The author has examined the components of *Anemone nemorosa*, *A. pratensis*, and *A. pulsatilla*.

Relation of Silver to the Chlorides and Bromides of the Alkali Metals.—J. S. Stas.—The author's determinations, taking O=16, are—K=39.1425, Na=23.0455, N=14.0550, Ag=107.9300. If we assume O:H=15.96:1, we have K=39.044, Na=22.988, N=14.019, Ag=107.660.

Equivalent Weight of Titanium.—T. E. Thorpe.—The mean value obtained is 48.013.

Atomic Weight of Platinum.—W. Halberstadt.—The author's mean result leads to the value 194.57592.

Moniteur Scientifique, Quesneville.
3rd Series, Vol. xvi., June, 1886.

Methylene Blue.—M. Bernthsen.—Translated from Liebig's *Annalen*.

The Manufacture of Toilet Soaps.—C. R. Alder Wright, F.R.S.—Translated from the *Journal of the Society of Arts*.

Industrial Review and Patents.—Extracts on the manufacture of ceresine from ozokerite (*Chemiker Zeitung*); on an alloy of 80 parts of lead with 20 parts of tin recommended in *Chemische Industrie* as resisting acids; on the influence of the composition of glass upon the variations of the thermometric scale, from the *Chemiker Zeitung*; on benzylmethylaniline and on a green colouring derivative, from the *Journal of the American Chemical Society* and abstracts of patents on improvements in smelting metals by means of electricity, by E. and A. Cowles; the preparation of white-lead by means of magnesium acetate and lead oxide, by Dr. W. Kubel; a process for deodorising mineral oils by treatment at a boiling heat with sulphurous acid, by Dr. A. Faulbaum; the preparation of a green colouring-matter by nitrating the Liebermann's phenolic colouring-matter; on an orchil-red azo colour; and on the use of the thiodiphenylamine and its ethyl and methyl derivatives for preparing colouring-matters.

Solubility of Antimony Oxide in Alkaline Solutions of Glycerine: New Mordant for Cotton-Dyeing.—Dr. Koehler.—The author dissolves caustic soda in an equal weight of distilled water, adds 100 grms. glycerin, and introduces antimony oxide, as a paste containing about 60 per cent of Sb₂O₃ until a notable quantity remains undissolved. The operation requires 1 hour, and the most suitable temperature is 80°. The antimony oxide used should be free from sulphide. This liquid is used as a substitute for tartar emetic in fixing tannin upon the fibre of cotton.

Germanium.—Dr. Quesneville.—The writer appeals to Dr. Winckler to give to his new element—here spoken of as a metal—the name of ekasilicon in place of germanium.

Notes on Cocaine and Hopeine.—From *Chemische Industrie* and the *Chemiker Zeitung*.

Analysis of the Fertilising Matters known as Commercial Manures.—This report has already appeared in the *CHEMICAL NEWS*.

Artificial Colouring Matters Applied in Industry.—The fifth of Prof. Noelting's course of lectures, describing the anthracene derivatives.

Properties and Proprietors of Ungreenable Aniline Black.—S. Grawitz.—A reply to a recent letter by M. Camille Kœchlin.

Bulletin de la Société Chimique de Paris.
Vol. xlv., No. 11, June 5, 1886.

Letter to the President of the Chemical Society.—P. Cazeneuve.—A brief controversial note on the use of metallic oxides for detecting coal-tar colours in wines.

On Two Properties of the Urethanes of the Fatty Series.—G. Arth.—Borneol and menthol carbamates do not form an exception to the general rule, but present the characters of other compounds of this class if studied in the same conditions.

Action of Alcoholic Potassa upon Urea, Sulphurea, and certain Substituted Ureas: A Reaction, the Inverse of that of Wœhler.—A. Halber.—Urea, both the natural product and the artificial kind, obtained by Wœhler's process if heated in sealed tubes with alcohol and potassa, is split up into potassium cyanate, ammonia, and water. Monoethylurea treated in the same manner is split up into potassium cyanate, ethylamine and water. Unsymmetric diethylurea yields potassium cyanate and diethylamine. Sulphurea forms ammonium sulphocyanide and sulphide, whilst a large part of the sulphurea remains unattacked.

On a Basic Copper Arseniate.—M. Coloriano.—The author has obtained the compound $\text{As}_2\text{O}_5\cdot 3\text{CuO}$ in slender laminæ or in isolated prisms.

Researches on certain Crystalline Arseniates.—M. Coloriano.—The author has obtained crystalline compounds of arsenic acid with zinc, manganese, and copper.

On Tellurous Anhydride and its Combinations with the Acids.—Daniel Klein.—The author examines the two varieties of tellurous anhydride, that prepared by the moist way and that crystallised by fusion. The former has the specific gravity 5.67, 5.65, 5.68, whilst the latter = 5.915. He has determined the crystalline form of tellurium nitrate; obtained and examined potassium hexatellurite and the double potassium and telluryl, sodium and telluryl, lithium and telluryl, and barium and telluryl tartrates.

Journal für Praktische Chemie.
New Series, Vol. xxxiii., Parts 10 and 11.

On the Constitution of the Platinum Bases.—S. M. Jörgensen.—This extensive memoir is quite incapable of useful abstraction within the space at our disposal.

A Contribution to our Knowledge of the Nature of the Setting of Cements.—Dr. E. Michel.—The author's experiments lead to the conclusion that the setting of cement depends: on the addition of water, which must be as moderate and as uniform as possible; on the density and on the most intimate mixture of the materials; on the formation of calcium carbonate. The proportion of lime for hardening needs to be but slight. All the three main constituents of cement, silica, alumina, and lime, are chemically active. Alumina determines the quick loosening and silica the permanent setting. Alkalies take no essential part in setting.

Two Reactions of Morphine.—Dr. J. Donath.—The first mentioned reaction is a completion of that of Tattersall (*CHEM. NEWS*, xli., p. 63), by means of sulphuric acid

and potassium arseniate. Finely-ground morphine (about 1 m.grm.) is well rubbed up with 8 drops of sulphuric acid in a porcelain capsule; a granule of potassium arseniate is added and stirred up together with the other materials. If the mixture is then heated over a small flame, shaking it all the time until acid vapours begin to escape, a fine violet blue colouration appears, which on further heating turns to a dark brownish red. On cautious dilution with water there appears a reddish colouration, which turns green on the further addition of water. If this liquid is poured into a test-tube, chloroform being added, and the whole shaken, the latter takes a splendid violet colour. Ether likewise takes a splendid violet-red, whilst the supernatant stratum is brown. Dehydromorphine, on the other hand, on rubbing up with sulphuric acid and potassium arseniate, becomes a dirty green, which turns brown on heating intensely green on dilution with water. This solution gives up no colouring matter to chloroform. The second reaction is effected with sulphuric acid and potassium chloride, and resembles the ferric-chloride reaction. A little morphine rubbed up with about 8 drops of strongest sulphuric acid turns grass green in the cold on adding a drop of a solution of 1 part of potassium chlorate in 50 parts concentrated sulphuric acid. The colour is very persistent, and at the margin of the liquid there appears a faint rose colouration. Dehydromorphine similarly treated becomes a brownish green.

On the Combustion - Heat of Benzol. — Julius Thomsen.

Reply to the Foregoing Memoir.—F. Stohmann.—A controversy with reference to certain experiments of H. F. Stohmann described in this Journal (vol. xxxiii., p. 241), each disputant taking exception to the method of the other.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Analyses of Two Samples of Rock-Salt from Northwich.—By ROWLAND WILLIAMS, F.C.S.—

	No. I. Per cent.	No. II. Per cent.
Sodium chloride.. .. .	99.761	99.247
Calcium.. .. .	0.094	—
Magnesium	0.145	0.213
Potassium	trace	trace
Sodium sulphate.. .. .	—	0.009
Calcium sulphate	—	0.082
Insoluble matter, clay, &c. ..	—	0.401
Organic matter	—	0.048
	100.000	100.000

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THE CHEMICAL NEWS.

VOL. LIV. No. 1392.

PROBABLE ISOLATION OF FLUORINE. DECOMPOSITION OF HYDROFLUORIC ACID BY AN ELECTRIC CURRENT.

By M. H. MOISSAN.

IN a former memoir* we showed that it was possible to decompose anhydrous hydrofluoric acid by the action of an electric current: at the negative pole hydrogen collects; at the positive pole a gaseous body is disengaged having novel properties. The experiment was performed in a platinum U-tube, closed by stoppers of fluorite, and having at the upper part of each branch a small delivery tube, also of platinum. Through the stopper passes a platinum rod, which acts as electrode; the metal employed for the positive pole is an alloy containing 10 per cent of iridium.

To obtain pure anhydrous hydrofluoric acid we begin by preparing fluorhydrate of fluoride of potassium, taking all the precautions pointed out by M. Frémy. When the salt is obtained pure it is dried on a water-bath at 100°, and the platinum capsule containing it is then placed in a vacuum in the presence of concentrated sulphuric acid, and two or three sticks of potash fused in a silver crucible. The acid and potash are renewed every morning for a fortnight, and the vacuum is kept at 2 c.m. of mercury. Care must be taken during this desiccation to pulverise the salt every day in an iron mortar, so as to renew the surface. When the fluorhydrate contains no more water it falls to powder, and is then fit to serve for the preparation of fluoric acid; the fluorhydrate of fluoride of potassium, if well prepared, is much less deliquescent than the fluoride.

When the fluoride is quite dry it is quickly introduced into a platinum alembic which has just been dried by heating it to redness. The whole is kept at a gentle temperature for an hour or an hour and a half, so as to allow the decomposition to commence very slowly; the first portions of acid which come over are rejected, as they carry with them traces of water remaining in the salt. The platinum receiver is then attached, and the heat increased, allowing the decomposition to proceed with a certain degree of slowness. The receiver is then surrounded with a mixture of ice and salt, and from this moment all the hydrofluoric acid is condensed as a limpid liquid, boiling at 19.5°, very hygroscopic, and, as is well known, giving abundant fumes in presence of the atmospheric moisture.

During this operation the platinum U-tube, dried with the greatest care, has been fixed with a cork in a cylindrical glass vessel surrounded with chloride of methyl. Up to the moment of introducing the hydrofluoric acid the leading tubes are attached to drying tubes containing fused caustic potash. To introduce the hydrochloric acid into the apparatus, it may be absorbed through one of the lateral tubes in the receiver in which it is condensed.

In some experiments we have directly condensed the hydrofluoric acid in the U-tube surrounded with chloride of methyl; but in this case care must be taken that the tubes are not clogged up by small quantities of fluoride carried over, which would infallibly lead to an explosion and projections, which are always dangerous with so corrosive a liquid.

When we have introduced in advance in the small platinum apparatus a determined amount of hydrofluoric

acid, cooled with chloride of methyl, in tranquil ebullition at a temperature of -23°, the current of 20 cells of Bunsen large size, arranged in series, is passed through by means of the electrodes. An ampère meter in the circuit admits of the intensity of the current being observed.

If the hydrofluoric acid contains a small quantity of water, either by accident or design, there is always disengaged at the positive pole ozone, which has no action on crystallised silicium. In proportion as the water contained in the acid is thus decomposed, it is seen by the ampère meter that the conductivity of the liquid rapidly decreases. With absolutely anhydrous hydrofluoric acid the current will no longer pass. In many of our experiments we have succeeded in obtaining an acid so anhydrous that a current of 25 ampères was entirely arrested.

To render the liquid conducting we have added before each experiment a small quantity of dried and fused fluorhydrate of fluoride of potassium. In this case decomposition proceeds in a continuous manner: we obtain at the negative pole hydrogen, and at the positive pole a regular disengagement of a colourless gas in which crystallised silicium in the cold burns with great brilliancy, becoming fluoride of silicium. This latter gas has been collected over mercury, and accurately characterised.

Deville's adamantine boron burns in the same manner, but with more difficulty, becoming fluoride of boron. The small quantity of carbon and aluminium which it contains impedes the combination. Arsenic and antimony in powder combine with this gaseous body with incandescence. Sulphur takes fire in it, and iodine combines with a pale flame, losing its colour. We have already remarked that it decomposes cold water, producing ozone and hydrofluoric acid.

The metals are attacked with much less energy. This is due, we think, to the small quantity of metallic fluoride formed preventing the action being very deep. Iron and manganese in powder, slightly heated, burn with sparks. Organic bodies are violently attacked. A piece of cork placed near the end of the platinum tube, where the gas is evolved, immediately carbonises and inflames. Alcohol, ether, benzol, spirit of turpentine, and petroleum take fire on contact.

The gas evolved at the negative pole is hydrogen, burning with a pale flame, and producing none of these reactions.

When the experiment has lasted several hours, and there is not enough hydrofluoric acid left at the bottom of the tube to separate the two gases, they re-combine in the apparatus in the cold, with violent detonation.

We have satisfied ourselves, by direct experiment, that a mixture of ozone and hydrofluoric acid produces none of the reactions described above.

It is the same with gaseous hydrofluoric acid. Finally we may add that the hydrofluoric acid employed as well as the hydrofluorate of fluoride were absolutely free from chlorine.

The gas obtained in our experiments is therefore either fluorine or a perfluoride of hydrogen.

New experiments are necessary to settle this last point. We hope soon to lay the results before the Academy.—*Comptes Rendus*, vol. ciii., p. 202, July 19, 1886.

Micro-organisms of Potable Water and their Life in Carbonated Waters.—T. Leone.—The fresh water from the Munich city works, which contains no traces of nitrites, nitrates, or ammoniacal salts, gives, per litre, a residue of 284 m.g., whilst the organic matter in the same quantity is oxidised by 0.99 m.g. of oxygen. This water contained, when fresh, only 5 microbes in 1 c.c.; in twenty-four hours the number had reached 100; in two days 10,500; in three days 67,000; in four days 315,000; and in five days more than half a million. In water saturated with carbonic acid the number of microbes, on the contrary, decreases.—*Biedermann's Centralblatt*, Pt. 3.

* *Comptes Rendus*, vol. cii., p. 1543, and *CHEMICAL NEWS*, vol. liv., p. 36.

THE REDUCTION OF FERRIC NITRATE IN THE NITROMETER.

By THOMAS BAYLEY.

I HAVE already stated that when ferric nitrate is shaken in the nitrometer with pure sulphuric acid a tint is produced which varies from "dark" port wine red to "reddish" or "pink," according to the amount of iron present. The term "raspberry," used by Prof. Lunge, expresses the tint very well for a certain stage of dilution. Prof. Lunge has obtained this tint by adding ferric nitrate to the liquid within the nitrometer, but has failed to discover any reduction to ferrous salt. He does not, however, offer any explanation of the appearance of the tint, nor any reason why it was not obtained in his second experiment. If it is not caused by a proto-salt of iron, what is the nature of the raspberry compound?

The colour produced with a ferric is identical with that which appears when a ferrous salt is directly employed, but in neither case is there any resemblance to a chocolate tint until after dilution with water. If crystals of nitre and ferrous sulphate are covered over with concentrated sulphuric acid in a test-tube the wine red or raspberry reaction is obtained: it is therefore not peculiar to the nitrometer.

With respect to the test for the ferrous salt with potassium ferricyanide, Prof. Lunge says:—"Of course, if the liquid were treated with that reagent just after being diluted, and therefore quite hot and containing an enormous excess of acid, it would turn blue with potassium ferricyanide, but no one acquainted with qualitative analysis will work that way." I am prepared to admit that this result is possible, but I have tried the experiment some half dozen times with concentrated acid and with mixtures of equal volumes of acid and water while still quite hot, without the production of a green or blue tint on any occasion.

This, however, is of no consequence in the present instance, as my tests have not been made in the way Prof. Lunge describes.

For the benefit of persons interested in qualitative analysis, it may be worth while to describe the exact process whereby the existence of the ferrous salt, and therefore the reduction of the ferric salt, can be demonstrated. If after the appearance of a dark raspberry tint the nitric oxide be expelled, and cold but recently boiled distilled water be added through the tap, the vitriol can be diluted without contact with air. If after cooling this dilute liquid is caused to flow along the channel drilled axially through the tap into a dilute and freshly-prepared solution of the ferricyanide of potassium, the blue colour instantly appears. The experiment can be repeatedly performed successfully when only a very few milligrammes of iron are present, if only a suitable quantity of ferricyanide be employed. Dilution of the vitriol while exposed to air occasions rapid and sometimes almost instantaneous oxidation, owing to the temperature and the presence of the oxide of nitrogen. I have by this method shown the reduction of ferric nitrate to several chemists, to their entire satisfaction.

One point alone remains for discussion, namely, whether commercial nitrous vitriol ever contains sufficient iron in any shape to dissolve a measurable quantity of nitric oxide. I am familiar with the working of seven chambers which are connected in series and have one Glover and one Gay-Lussac tower. The acid from the absorber circulates of course through the Glover and the excess is passed into certain chambers of the series. On the 19th inst. a sample of the Glover acid was nitrous, and 8 c.c. of it gave the tint of a dark ripe raspberry and liberated 3.0 c.c. of nitric oxide. After expelling the gas and leaving the liquid standing over the mercury for 24 hours no more oxide of nitrogen was liberated on further shaking. But on adding about 8 c.c. of water gas was evolved which

measured 5 c.c. when cold. The liquid was now of chocolate colour, and judging from my former experiments probably contained 1 c.c. of gas. The amount set free by water was thus one-sixth of that disengaged by the first shaking and was certainly a measurable quantity. This sample of Glover acid was doubtless similar to those described in Prof. Lunge's book on alkali as depositing a crust of ferric nitrate during concentration, but even where the amount of iron is smaller and the extra gas hardly measurable, it does not follow that the dissolved portion is quite insignificant in amount. Prof. Lunge has now "closed his account in this matter" of the nitrometer, but doubtless still "lives to fight another day" with a more worthy adversary; and I am fain to close my account too, but not without an expression of thanks to the editor of this journal for the opportunities of discussion he has so liberally afforded, and to Prof. Lunge for the patient manner in which he has contributed to the controversy since my original statement of fact.

VERIFICATION OF THE CALCULATION OF THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

TWENTY-FIVE years ago M. Stas commenced publishing the results of his researches on the atomic weights of silver and some other bodies. Five years later, that is in 1865, in an extended memoir which M. de Marignac described as beautiful, magnificent, immense, he completed and amplified these estimations. Having submitted the wet method of Gay-Lussac to a fresh examination, M. Stas published his researches on the chloride and bromide of silver, the study of which, in spite of its difficulty, is indispensable in order to properly appreciate his "Memoir on the Proportional Relation between Silver and its Chlorides and Bromides." This last work, although presented to the Academy of Brussels in 1876, was not printed until six years afterwards.

This paper is very little known, and I have never seen it quoted, although several previous estimations are corrected therein.

I have often studied and consulted these works on account of the numerous details they furnished me with for my own experiments on the atomic weights of carbon, phosphorus, zinc, tin, and hydrogen.† The verification to which I have submitted the calculations of M. Stas seems superfluous, seeing that it deals with the experiments of a *savant* who has never had an equal in exactitude. It may perhaps astonish some as much as it did me to find that the original memoirs contain numerous arithmetical mistakes as well as typographical errors, of which some are considerable.

In his first published paper M. Stas gives a table of atomic weights, the result of his researches, but he says hardly a word of the method of arriving at them. In the two other memoirs we find further details on that point, but as these books have been written in parts at different times they do not treat the subject in a general manner. Nobody has yet gone over the calculation of the complete system of these estimations, which fact encourages me to publish this essay.

It is part of a long tedious work which comprises all the simple bodies. According to the recent works of MM. Becker, Clarke, Meyer and Seubert, Sebelien and Oswald, the detail and publication of these calculations would be useless. I will therefore only communicate my results, that is to say, the atomic weights which seem to me to be most reasonable, and the uncertainty which still exists about each.

* *Ann. Chim. Phys*, 6th Series, vol vii., April, 1886.

† A preliminary notice is inserted in the *Comptes Rendus de l'Académie des Sciences*, Jan. 5, 1885, vol. c., pp. 52 and 1175.

Table of Atomic Weights according to M. van der Plaats.

	Atomic weights.	Degree of uncertainty.
Ag	107.93	0.01
Al	27.08	0.05
As	75.0	0.3
Au	196.7	0.5
Ba	137.1	0.1
Bi	208.0	0.3
Bo	11.0	0.1
Br	79.955	0.01
C	12.005	0.005
Ca	40.0	0.05
Cd	112.1	0.2
Ce	141.5	1.0
Cl	35.456	0.005
Co	58.8 or 60.0	0.5
Cr	52.3	0.3
Cs	132.8	0.3
Cu	63.33	0.02
Di	145.0	3.0
Er	166.0	2.0
F	19.0	0.1
Fe	56.0	0.05
Ga	70.0	1.0
Gl	9.1	0.2
H	1.00	0.005
Hg	200.1	0.2
In	113.7	0.5
Ir	193.0	0.2
I	126.86	0.01
K	39.144	0.01
La	138.0	2.0
Li	7.02	0.01
Mg	24.4	0.05
Mn	55.0	0.1
Mo	96	0.3
N	14.05	0.01
Na	23.05	0.005
Nb	94.0	2.0
Ni	58.0 or 58.8	0.5
O	16	Basis.
Os	195	5.0
P	30.95	0.05
Pb	206.91	0.05
Pd	106.5	1.0
Pt	194.9	0.2
Rb	85.4	0.1
Rh	104.0	1.0
Ru	104.0	1.0
S	32.06	0.01
Sb	120.0	0.2
Sc	44.0	0.5
Se	79.0	0.2
Si	28.0	0.1
Sm	150.0	0.5
Sn	118.1	0.1
Sr	87.5	0.1
Ta	182.8	0.5
Te	125.0	3.0
Th	233.0	1.0
Ti	48.1	0.1
Tl	204.2	0.5
U	240.0	1.0
V	51.3	0.1
W	184.0	0.2
Y	89.5	1.0
Yb	173.0	1.0
Zn	65.3	0.1
Zr	90.5	1.0

I must hasten to say that this is the only point on which I could venture to correct or control the work of the illustrious *savant* at Brussels. Having devoted several years to similar researches, I am the more able to appreciate the vast difference which separates the estima-

tions of atomic weights of other chemists from those of M. Stas.

The remarks and corrections which I am about to make are founded entirely on the observations and data given by M. Stas himself.

As we have to deal sometimes with the determination of the third decimal, I have calculated the fourth. As I used logarithms of seven decimals, the seventh figure may be, at the most, one or two units wrong. All my calculations have been done twice and then verified; I hope therefore that they are exact.

(To be continued).

NOTE ON WATER OF CRYSTALLISATION.

By W. W. J. NICOL, M.A., D.Sc.

WHEN a hydrated salt is dissolved does it retain its water of crystallisation, or does this latter cease to be distinguishable from the solvent water? Both views have found advocates among chemists who have looked at the question of solution, and both have been supported by arguments more or less to the point. But among the possible means of solving this question there is one which has entirely escaped the notice of those interested in the subject. And those who hold that water of crystallisation exists in solution have been entirely oblivious of the fact that, while they are ready to accept the results of the modern science of thermo-chemistry and to employ them to support their views on hydration, yet these very results if correct prove without a shadow of a doubt that water of crystallisation does not exist in solution.

The proof is so clear and self-evident when once one's attention is directed to it, that, though I intend to develop it more fully on another occasion, I feel that it is better to publish an outline of it at once.

Thomsen has found that the heat of neutralisation of the soluble bases of the alkalis and alkaline earths with sulphuric acid has a mean value of 31.150 c. within very narrow limits. When hydrochloric or nitric acid is employed the value is 27.640 c., also within very narrow limits. Now this agreement of the six bases in their behaviour with sulphuric acid, much more of the seven bases with both HNO_3 and HCl , is so close that it cannot be regarded as accidental, but, in the words of Meyer, the heat of formation of a salt in aqueous solution is a quantity made up of two parts, one a constant for the base, the other for the acid. But of the 20 salts thus formed some are anhydrous in the solid state, others have water of crystallisation, up to 10 molecules in the case of Na_2SO_4 . If water of crystallisation exists in solution it will be necessary to suppose that this agreement is accidental, which is absurd, as a glance at the probabilities will show. Thomsen himself expressly states that he regards the dissolved state as one in which the conditions are comparable for all substances: this would be impossible if water of crystallisation were present.

A still stronger proof is afforded by the "avidity" of Thomsen or the "affinity" of Ostwald—both have worked on the subject, taking no account of water of crystallisation, and the results, *e.g.*, for H_2SO_4 and HCl with NaHO , where water of crystallisation *may* come in, are entirely confirmed by Ostwald's results on inversion and etherification, where there can be no water of crystallisation.

The proof is complete, water of crystallisation cannot be attached to the salt in solution, or if it is no heat is evolved on union more than with solvent water. The alternative is to suppose that the whole of the above thermo-chemical results are coincidences.

On Dehydromorphine.—Dr. Julius Donath.—Dehydromorphine, tried in quantities of 0.5—1.5 grm., could be reduced to morphine neither by sodium amalgam in an alkaline solution nor by zinc or tin in an acid liquid.

ON RADIANT MATTER SPECTROSCOPY.*

PART II.—SAMARIUM.

By WILLIAM CROOKES, F.R.S.

(Continued from p. 43).

Purification of Samaria.

133. THE foregoing experiments left little doubt that *x*, the orange-band-forming body, was samarium; the last problem was, therefore, to get this earth in a pure state. The general plan of operations was the same as I adopted in getting didymium free from samarium, only attention was now directed to the portions richest in samarium which had been formerly set aside (128, 129). On fractionation in highly dilute solutions with very weak ammonia the first precipitates are richer in samaria than the last. These first precipitates were re-converted into nitrates, and fractionation again proceeded with.

Fusion of the nitrates with potassic nitrate (129), or precipitation by, and washing with, potassic sulphate (130), are of no use in the final purification of samarium. When the object is to separate a little samarium from a large quantity of didymium, fusing the nitrates will effect the purpose, but I have not found the converse to hold good. The potassic sulphate method cannot separate the last traces of didymium from samarium, for the didymic double sulphate, not being quite insoluble, would wash out along with the first portions of the samaric salt. I have found no method better than fractionation with ammonia, and Prof. Clève tells me that is his experience.

Towards the end of the operations, when the samaria is getting pure, it is useful to precipitate it as a double sulphate with potassic sulphate, and wash it well for some time, to remove any traces of earths of the yttria and other groups which might have been present and become accumulated with the samaria (123).

134. During fractional precipitation with ammonia an experienced eye can judge roughly what is the preponderating earth present, by the appearance of the precipitate as it comes down. When much samaria is present, with but little didymia and lanthana, the precipitate forms immediately. When there is much didymia, and little samaria and lanthana, the precipitate forms almost as quickly as in the first case, but does not settle so rapidly. With much didymia, and a fair quantity of lanthana, the precipitate forms more slowly than before and settles sluggishly. When there is much lanthana and little didymia the precipitate takes a long time to settle, the liquid remaining opalescent for days. These peculiarities are due in great measure to the varying basicity of the elements, samarium being the least basic and lanthanum being the most basic, didymium occupying an intermediate position.

In freeing samarium from the last portions of didymium the only test available to detect the presence of the latter metal is the absorption spectrum. The best plan is to provide a strong solution of the samaric nitrate in a flask, to act as a lens, and to concentrate the light of a gas-flame by its means on to the slit of a low dispersion spectroscop. Long after the light colour of the ignited oxide shows that the didymium is getting small in quantity, its absorption bands will be so strong as almost to obliterate the fainter samarium spectrum.

135. The fractionation should be persevered in till no didymium bands are seen in the absorption spectrum. After this point is reached I prefer to keep on fractionating for some time longer, if the material will hold out, so as to make assurance doubly sure. The colour of samaria, as pure as I have been able to prepare it, is white with the faintest possible tinge of yellow. The absorption spectrum of samarium salts is much more feeble than the spectrum of didymium salts.

The accompanying drawing (Fig. 2) shows the absorption spectra of solutions of didymic and of samaric

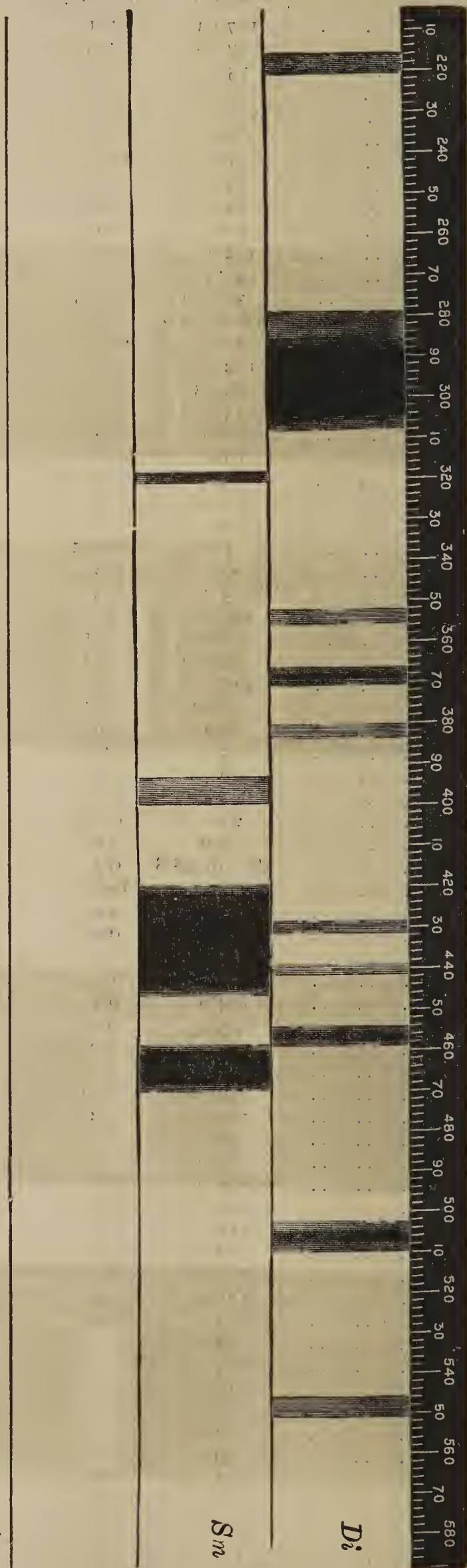


FIG. 2.

nitrates. It will be observed that the strongest bands of the samarium absorption spectrum are almost covered by strong absorption bands of didymium. Unless, therefore, the samarium is decidedly in excess, it will be difficult for any but a very practised observer to detect its presence. Fortunately the marvellous delicacy of the phosphorescent

* A Paper read before the Royal Society, June 18, 1885.

spectrum of samarium renders any other spectrum test of little value.

136. I have already mentioned (117) that the cerite earths are supposed to contain a fifth member, which has been provisionally called *Ya*.* Not much is known respecting the properties of this earth, but from the little I can glean it would appear to become concentrated with the samarium, from which a partial separation may be

trum in the radiant-matter tube. Whether or no it was *Ya* I cannot say, as the quantity obtained was insufficient to enable me to determine its atomic weight.

The Phosphorescent Spectrum of Samarium.

137. Pure samaric sulphate by itself gives a very feeble spectrum. Some of the pure salt was heated to redness,* sealed in a radiant-matter tube, and carefully exhausted.

FIG. 3.

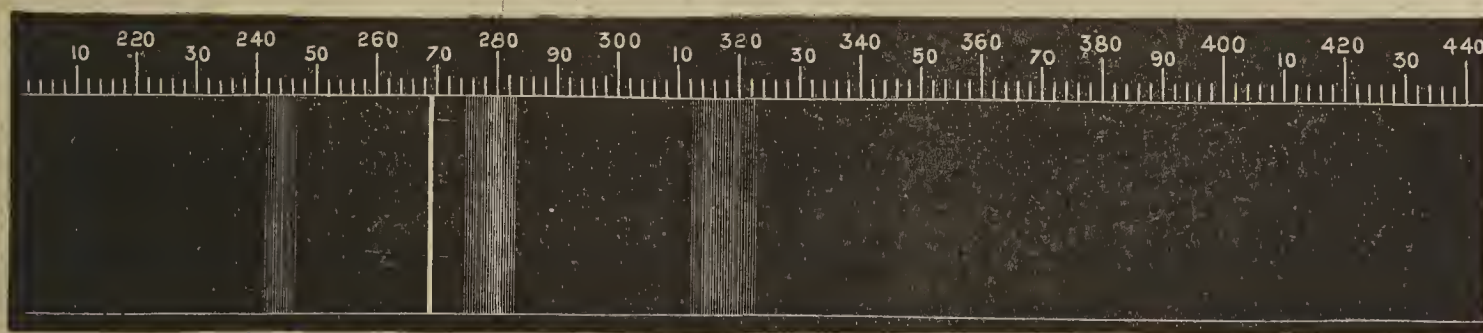
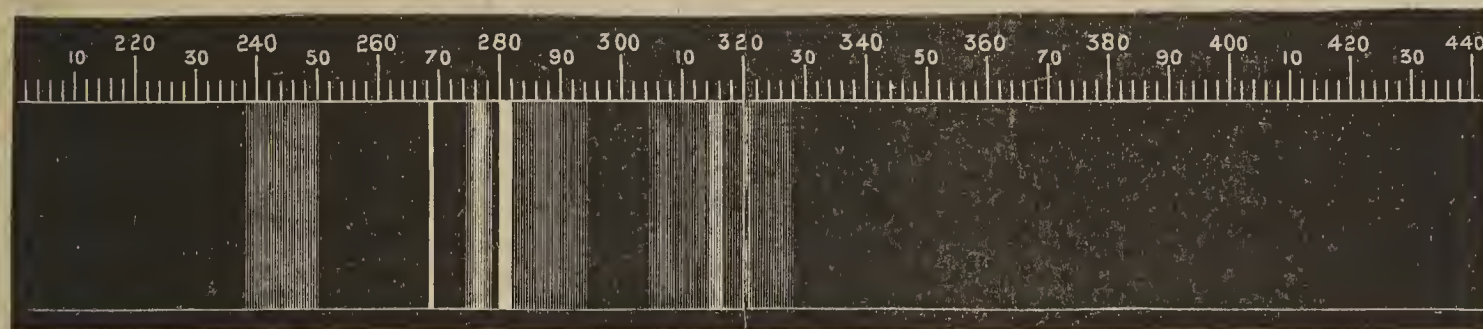


FIG. 4.



effected either by continuing the operation of fractional precipitation or by taking advantage of the different solubilities of their double potassic sulphates in potassic sulphate; the potassio-samaric sulphate being almost

The coil was adjusted so as to give a powerful spark; the room was well darkened, and the eye kept shielded from extraneous light. It was difficult to hit the exact moment of exhaustion between the disappearance of gas and non-

FIG. 5.

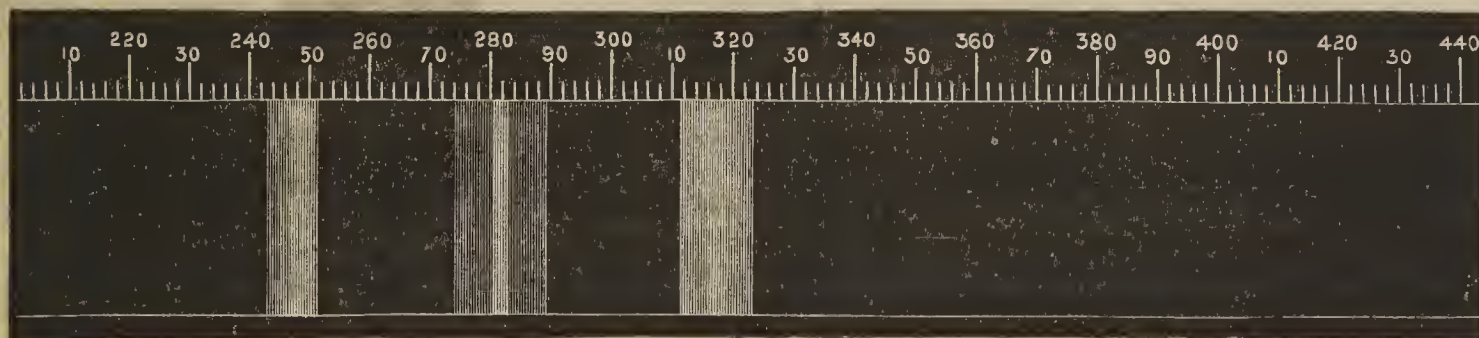
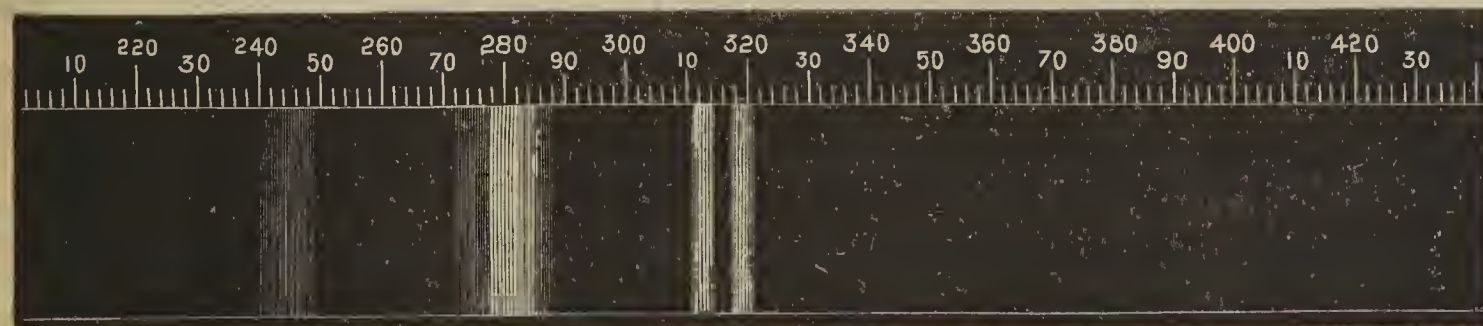


FIG. 6.



insoluble in a saturated solution of potassic sulphate, whilst the corresponding salt of *Ya* is soluble in 100 to 200 volumes of the same solution. By persevering in this mode of treatment I ultimately obtained a small quantity of a white earth which gave no samarium spec-

conductivity, but by careful watching at the spectroscope a point was reached at which the phosphorescence appeared. The spectrum consists of a faint band in the red, then a sharp orange line (146, 165), next a wide ill-

* Marignac, *Comptes Rendus*, vol. xc., p. 899; CHEMICAL NEWS, vol. xli., p. 250.

* Samaric sulphate is not decomposed at the temperature employed.

defined orange band, and finally an equally ill-defined green band. The appearance is shown in Fig. 3.

138. When, however, the samaria is mixed with lime (114) before examination in the radiant-matter tube, the change is very striking, and the spectrum is, if anything, more beautiful than that of yttrium. The bands are not so numerous, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, which require care to bring them out, the spectrum is seen to consist of three bright bands,—red, orange, and green,—nearly equidistant, the orange being the brightest. With a narrower slit the orange and green bands are seen to be double, and on closer examination faint wings are seen, like shadows to the orange and green bands. In this spectrum the sharp orange-coloured line (137) of pure samaric sulphate is absent.

139. The bands are best seen in a spectroscop of low dispersion, and with not too narrow a slit. In appearance they are more analogous to the absorption bands seen in solutions of didymium than to the lines given by spark spectra. Examined with a high magnifying power all appearance of sharpness generally disappears: the scale measurements given below must therefore be looked upon as approximate only; the centre of each band may be taken as accurately determined within the unavoidable errors of experiment, but it is impossible to define their edges with much precision.

140. The accompanying cut (Fig. 4) gives as good an idea of the spectrum of samarium-calcium as is possible in black and white. The numbers along the top are the squared reciprocals of wave-lengths, and are on the same scale as the diagram of the yttrium spectrum (71) given in my Bakerian Lecture already quoted. The phosphorescing mixture in the tube consisted of 20 parts of pure samaria and 80 parts of lime. They were converted into nitrates in a platinum capsule, and then decomposed by excess of sulphuric acid and ignited at a dull red-heat. If sulphuric acid is added in the first instance there is a difficulty in getting the earths completely converted.

The least refrangible band seen is a very faint red, which extends from $\frac{1}{\lambda^2}$ 2310 to 2400. Here a much stronger red band begins extending to 2494. The first component of the bright orange band begins at 2739 and ends at 2762. Between 2762 and 2798 is a dark interval, and then the second component of the orange band is seen extending from 2798 to 2818. This band is stronger and more sharply defined than the preceding band. A faint yellow wing extends from the second orange band to 2942. There is now an intensely black interval reaching to 3025; here a faint yellowish green light is seen extending to 3149, where the green band commences and extends to 3164. Here a fainter green wing begins, and extends to 3270. On this wing a very narrow faint green band is seen, having its centre at 3190. There is then another dark space, after which three ill-defined blue and violet bands are seen, too faint to measure accurately.

141. Preliminary experiments (114) had shown me that lime was one of the best materials to mix with samaria in order to bring out its phosphorescent spectrum, but it was by no means the only body which would have the desired effect. More accurate observations were now taken with pure materials mixed together in definite quantities. The bodies employed were those enumerated in par. 113. Of these the following induced no phosphorescence:—zirconium, cerium, didymium, copper, silver, manganese, and tin; silicic, titanitic, tungstic, molybdic, niobic, and tantalic acids.

142. The other substances which I tried caused the samarium to give good phosphorescence with a discontinuous spectrum. There is a general resemblance between these spectra, but nearly all of them differ one from another in details. In the following descriptions I will take the calcium-samarium spectrum (140) as the standard of comparison:—

Strontium and barium, when mixed with samarium, give almost identical spectra; the red band is similar to the one produced by calcium, but the orange bands have become a blurred orange space, with outline ill-defined on the side towards the red, and sharper at the more refrangible side. There is no trace of division in the orange space; but the green, which with calcium is narrow and single, becomes with barium and strontium a well-defined luminous double green band, with a sharp black separating interval.

Beryllium and samarium give a very faint phosphorescent spectrum, consisting of a red, orange, and green band only; the green occupying the position of the second green band given by calcium-samarium.

143. Thorium and samarium give a very similar spectrum to the one produced by barium or strontium with samarium, a slight difference being observable in the orange, which shows signs of separation into two components.

Thorium, as oxide or sulphate, by itself gives no phosphorescence (26, 28), and in fact, as I have already shown, renders the vacuum tube non-conducting;* samaria likewise gives scarcely any phosphorescence (137). It is, therefore, somewhat remarkable that a mixture of these two bodies should bring out the samarium spectrum so brilliantly.

Magnesium and samarium give the red band and second orange band sharply; the first orange is, however, obliterated, and its place occupied by a faint, broad, ill-defined band, extending to the orange band. The green band is very wide, faint, and ill-defined.

Zinc and samarium give the red band as usual, but there is only one orange band, which is sharp, and occupies the position of the interval between these bands in the calcium and samarium spectrum. The green band is widened out, and occupies the position of the second green band of the thorium-samarium spectrum.

The cadmium-samarium spectrum is similar to that of zinc-samarium, only the green band is still wider, and extends further towards the red end.

144. Lead with samarium gives a very brilliant spectrum. The red is clear and sharp, and has a narrow faint wing on each side. The orange is one wide band, with no trace of division, whilst the green is sharp and duplicated as in the thorium-samarium spectrum, to which, indeed, it bears a great resemblance. The centres of the green bands are at $\frac{1}{\lambda^2}$ 3133 and 3199.

Lanthanum and samarium phosphoresce brightly, and give a very sharp spectrum consisting of three bands, closely resembling the zinc-samarium spectrum; the red, however, not being so bright as the other two bands. On the contrary, cerium or didymium mixed with samarium gives no phosphorescence.

Aluminium and samarium give a spectrum resembling the corresponding calcium one as to the red and double orange, but having a very broad, somewhat faint, green band, with a black division in the middle occupying the position of the bright green band of calcium-samarium.

Bismuth and samarium gave a somewhat faint spectrum, almost identical with the lanthanum-, zinc-, cadmium-, and glucinum-samarium spectrum.

The antimony-samarium spectrum is almost identical with that with bismuth, the spectrum being, however, much fainter.

145. The samarium spectra, modified by other metals as above described, may be divided into three groups. The

* "This earth is, however, remarkable for its very strong attraction for the residual gas in the vacuum tube. On putting thorina in a tube furnished with well-insulated poles, whose ends are about a millimetre apart in the centre, and heating strongly during exhaustion, the earth, on cooling, absorbs the residual gas with such avidity that the tube becomes non-conducting, the spark preferring to pass several inches in air rather than strike across the space of a millimetre separating the two poles."—*Proc. Roy. Soc.*, No. 213, 1881, vol. xxxii., p. 209.

first group comprises the spectra given when glucinum, magnesium, zinc, cadmium, lanthanum, bismuth, or antimony is mixed with the samarium. It consists simply of three coloured bands, red, orange, and green; as a typical illustration I will select the lanthanum-samarium spectrum (Fig. 5). The centres of the bands are—red 2429, orange 2808, and green 3177.

The second type of spectrum gives a single red and orange and a double green band. This is produced when barium, strontium, thorium, or lead are mixed with samarium. The lead-samarium spectrum (Fig. 6) illustrates this type. The centres of the bands of this spectrum are—red 2437, orange 2830, green 3133 and 3199.

The third kind of spectrum is given by calcium mixed with samarium. Here the red and green are single, and the orange double. Aluminium would also fall into this class were it not that the broad ill-defined green band is also doubled. The calcium-samarium spectrum, already illustrated in Fig. 4 (140) is a good illustration of this type.

(To be continued.)

ON THE SO-CALLED SILVER SUB-CHLORIDE.

By SPENCER B. NEWBURY.

A YEAR ago I published a series of experiments* on the action of solvents on silver chloride which had been blackened by exposure to light, from which the conclusion was drawn that in the blackening action of light no silver sub-chloride, but only metallic silver, is formed. This was shown to be the case by the fact that if blackened silver chloride be treated repeatedly with a concentrated solution of sodium chloride, the silver chloride which has escaped reduction is completely dissolved, and pure, finely divided metallic silver remains.

The existence of silver sub-chloride has generally been assumed by chemists and writers on photography, and the formula Ag_2Cl has been supposed to represent its composition. A very complete outline of the literature of the subject is given by Von Bibra,† and need not be repeated here. There may be said to be three methods by which the so-called silver sub-chloride has been prepared, as follows:—

1. Cavillier,‡ by passing excess of chlorine into an ammoniacal solution of silver chloride.
2. Wetzlar,§ by action of iron or copper chloride on metallic silver.
3. Wöhler,|| by the action of hydrochloric acid on silver sub-oxide or its salts.

In the last case Wöhler prepared silver sub-citrate by heating silver citrate to 100° in a current of hydrogen: he expressly states, however, that the existence of this substance is not proved, since a mixture of metallic silver with undecomposed citrate would behave in a similar manner. By treatment of the sub-chloride with potash and hydrochloric acid respectively, Wöhler obtained the corresponding silver sub-oxide and sub-chloride. No attempts seem to have been made to free these substances from possible admixtures of metallic silver or from unchanged citrate or chloride, in order to render the analysis of them conclusive. Von Bibra¶ prepared the so-called sub-chloride by the three methods given above, and concluded that No. 1 gives true sub-chloride; No. 2, a mixture of silver and silver chloride; No. 3, also true sub-chloride. In the last case Von Bibra assumed the reaction to be complete when the weight of the silver

citrate, after heating six to seven hours in a current of hydrogen, remained constant; washed the product with water to remove free citric acid, treated with HCl , assumed the product to be pure silver sub-chloride, and established its formula to be Ag_4Cl_3 .

In the hope of preparing the sub-chloride in a pure state by the action of some solvent which should remove possible impurities, I was led to make the following experiments:—

1. The method of Cavillier, by action of chlorine on ammoniacal silver solutions, was tested. A stream of dry chlorine was conducted into a solution of silver chloride in ammonia. A slight grey precipitate was gradually formed, which, if the solution was kept strongly ammoniacal, consisted of finely divided silver wholly soluble in nitric acid. If, however, the ammoniacal solution was allowed to become nearly saturated with chlorine, mixtures of silver chloride and metallic silver, in varying proportions, were deposited, which on treatment with NaCl left a residue of grey metallic silver. From this I conclude that no sub-chloride is formed by this reaction. This is not remarkable, since all authorities agree that the hypothetical sub-chloride is decomposed by ammonia, silver chloride being dissolved, and metallic silver remaining. The formation of the sub-chloride in a strongly ammoniacal solution was therefore not to be expected. The precipitation of a small quantity of metallic silver is perhaps owing to impurities in the chlorine which exercise a reducing action.

2. Finely divided silver was treated with a cold 20 per cent solution of cupric chloride. Cuprous chloride was at once formed, but re-dissolved on addition of large excess of cupric chloride solution, leaving only white silver chloride.

If a few drops of stannous chloride solution are added to a solution of silver nitrate, a precipitate is formed which is at first white, but becomes black on stirring. Analysis of this precipitate showed silver and chlorine in varying proportions. If, however, stannous chloride be added in excess, a white precipitate consisting of silver chloride and a tin compound, probably oxychloride, is formed. If, therefore, dilute silver nitrate solution be gradually added to dilute stannous chloride solution until a dark precipitate begins to form, the precipitate then filtered off, and a further addition of silver nitrate made to the filtrate, a black precipitate is obtained. This was found to be metallic silver. It is evident that it is the stannous nitrate formed in this reaction which reduces the silver after all the chlorine has been precipitated, and also that no silver sub-chloride is formed.

3. I have made a large number of careful experiments on the preparation of silver sub citrate by heating silver citrate to 100° in a current of hydrogen, following exactly the instructions of Wöhler and Von Bibra. The hydrogen was passed through a red-hot tube, and dried with sulphuric acid and calcium chloride. The silver citrate was very carefully dried in vacuum. Nevertheless I did not find it impossible to obtain a constant weight as described by Von Bibra, nor to obtain a product of definite composition. Water was always given off, and a gradual decrease in weight took place, more or less rapid according to the rapidity of the stream of hydrogen. The silver citrate was changed to a black powder, under the action of a moderate current of gas, in about two hours, and was then found to have lost about 2 per cent of its weight. If the action was continued several hours longer the mass appeared to be partly fused, had a metallic lustre, and was found in some cases to have lost weight to the amount of 6 per cent. On treating the product with water a solution resulted which was red by transmitted light, but invariably grey and cloudy by reflected light. It seems to me highly probable that this red colour is caused by finely divided metallic silver. Hydrochloric acid produces in the solution a reddish precipitate, which on analysis was found to consist of silver chloride, with a minute amount of free silver. This shows that even when the

* *American Chemical Journal*, vol. vi., No. 6.

† *Journ. f. Prakt. Chem.*, 1875.

‡ *Journ. d. Pharm.*, 1830.

§ *Fahresber.*, 1828.

|| *Ann. Chem. Pharm.*, xxx.

¶ *Loc. cit.*

action of the hydrogen is continued for several hours there is still a large amount of unchanged citrate present. I have made many attempts to separate the constituents of this black substance by solution in water, but obtained no results, because the red solutions are not clear, and give only silver chloride and traces of silver on treatment with HCl. It is evident that the statement generally contained in the text-books, that the argentous citrate dissolves in water with a red colour, is incorrect.

On treating the black powder directly with hydrochloric acid, curdy brown precipitates were obtained, which contained varying proportions of silver and silver chloride, according to the duration of the action of the hydrogen. The substances were analysed by dissolving out the silver chloride by ammonia, and weighing residue of metallic silver. The formula Ag_4Cl_3 requires AgCl 81.8 per cent, Ag 18.2 per cent; Ag_2Cl requires AgCl 57.1 per cent, Ag 42.9 per cent. Varying proportions of silver were found, according to the length of time treated. In some cases the amount of silver was found to exceed 60 per cent.

The substances obtained by acting upon the reduced citrate with hydrochloric acid were treated with cold solution of sodium chloride. In every case silver chloride was dissolved, and a residue of metallic silver was left. Wöhler, in the article referred to above, states that ammonium chloride solution produces this result. It is therefore evident that if the sub-chloride exists it is of so unstable a character as to be readily decomposed by the ordinary solvents of silver chloride. There is, in fact, no evidence whatever of the existence of such a compound, or that the substances which have been supposed to be silver sub-chloride are anything but simple mixtures of silver and silver chloride.

In the case of the sub-citrate and sub-oxide the fact that Wöhler and Von Bibra obtained a product of constant weight on heating silver citrate in hydrogen has been assumed to be a proof of the existence of these substances. However, the hypothesis of the formation of silver sub-citrate does not account for the loss of weight which has been in every case observed. The replacement of silver by hydrogen, and setting free of citric acid, calls for a gain in weight.

In my own experiments, which have been very numerous, and performed under a variety of conditions, an absolutely constant weight was in no case obtained. Both water and carbon dioxide were given off, in approximately equal quantities, as long as the action of the hydrogen was continued. On exhausting the products with ether a brown tar-like mass was obtained, which contained free citric acid in considerable quantity, together with other substances which were not identified.

In conclusion, the loss of weight on heating silver citrate in a current of hydrogen, the formation of carbon dioxide, and residue of metallic silver left on treating the products with sodium chloride solution, seem to me to indicate that the reaction in question consists in the separation of silver and decomposition of citric acid, rather than in the formation of silver sub-citrate.—*American Chemical Journal*, Vol. viii., No. 3.

Poisoning by Aniline at Bâle.—M. Bruhat.—In France iron filings and acetic acid are generally employed for producing the hydrogen required for the reduction of nitro-benzol to aniline. In Sott Bâle a well-known firm had been using hydrochloric acid instead of acetic acid, and had obtained a quantity of hydrochloric acid from Giessen, said to have been made with strongly arsenical sulphuric acid. The arsenic chloride present was converted in the process into arsenic hydride. The lives of five of the workmen were saved with great difficulty. The question is raised whether coal-tar colours may not be rendered poisonous in this manner, though no arsenic acid has been knowingly used in their manufacture.—*Journ. de Pharm.*

COHESION AND COHESION FIGURES.*

By WILLIAM ACKROYD, F.I.C.

1. A Law of Solubility.

It is customary to regard cohesion as the force which binds together molecules of the same substance, and in virtue of which the particles of solids and liquids are kept together, and also to speak of the attraction exerted between particles of two different bodies as adhesion. The distinction between cohesion and adhesion is a conventional one. The similarity, if not identity, of the two forces is demonstrated by the fact that while cohesion is exerted between particles of the *same* body, adhesion is exerted with most force between particles of *allied* bodies. Generally speaking, organic bodies require organic solvents; inorganic bodies, inorganic solvents. For example, common salt is highly soluble in water but not in ether, and many fats are soluble in ether but not in water. So many cases like these will suggest themselves to the chemist that I am justified in making the following generalisation:—*A body will dissolve in a solvent to which it is allied more readily than in one to which it is highly dissimilar.* Exceptions to the law undoubtedly exist, but none so striking as the following in support of it, viz., that the metal mercury is the only known true solvent for many metals at the normal temperature.

2. Its Connection with Mendeleeff's Periodic Law.

From this standpoint the whole subject of solution is deserving of fresh attention, as it appears highly probable that, just as Prof. Carnelley has shown, by the use of my meta-chromatic scale that the colours of chemical compounds come under definite laws, which he has discovered and formulated in connection with Mendeleeff and Newland's periodic law,† so, likewise, may the solubility of an allied group of compounds, in regard to any given solvent under constant conditions of temperature, conform to similar laws; that, e.g., the chlorides of H, Na, Cu, and Ag in Mendeleeff's Group I. may vary in their solubility in water from an extreme of high solubility in the case of hydrogen chloride to the opposite extreme of comparative insolubility in the case of silver chloride. In this natural series of compounds hydrogen chloride is the body nearest akin to water, and silver chloride the most remote in kinship.

3. A Solidified Vortex Ring.

It is in virtue of cohesion that a freely suspended drop of liquid assumes the spherical form. If such a sphere be dropped on to the surface of a liquid of higher specific gravity at rest, one obtains what is called the cohesion figure of the substance of the drop. A drop of oil, e.g., spreads out on the surface of water until it is a circular thin film of concentric rings of different degrees of thickness, each displaying the characteristic colours of thin plates. The tenuity of the film increases; its cohesion is overcome; lakelets are formed and they merge into each other. The disintegrated portions of the film now thicken, the colours vanish, and only islets of oil remain. Some liquid drops of the same or higher sp. gr. than water do not spread out in this fashion but descend below the surface of the liquid, and, in descending, assume a ring shape which gradually spreads out and breaks up into lesser rings. Such figures have been termed submergence cohesion figures; they are vortex rings. I have solidified such vortex rings in their first stage of formation. If drops of melted sulphur at a temperature above that of the viscous state be let fall into water the drops will be solidified in the effort to form the ring, and the circular button, thick in the rim and thin in the centre, may be regarded as a solidified vortex ring of plastic sulphur.

* Notes from a Lecture given to the Halifax Scientific Society, July 19, 1886.

† *Philosophical Magazine*, August, 1884.

4. That a Submergence Cohesion Figure is a Vortex Ring.

It may be shown that the conditions of the formation of a submergence cohesion figure are those which exist in the formation of an aerial vortex. Those conditions in their greatest perfection are (1) a spherical envelope of a different nature from the medium in which the rings are produced, (2) a circular orifice opening into the medium, and (3) a percussive impact on the part of the sphere opposite the orifice. In the production of vortex rings of phosphorus pentoxide in the making of phosphoretted hydrogen, the spherical envelope is water, the orifice the portion of the bubble which opens into the air immediately it rises to the surface, and the impact is furnished by gravity. So, also, in the case of a submergence cohesion figure, the spherical envelope is the air surrounding the drop, the orifice the portion of it which first comes in contact with the liquid at rest, and here again the impact is due to gravity more directly than in the former case. These conditions are somewhat imperfectly copied in the ordinary vortex box, which is usually cubical in form, with a circular orifice in one side and a covering of canvas on the opposite one, which is hit with the fist.

ON DINITROSULPHOCYANBENZENE.*

By PETER T. AUSTEN and FRANKLIN S. SMITH.

CLEMM† found that when trinitrochlorbenzene was treated with potassium sulphocyanide an energetic action ensued and a well-characterised compound was formed. He was unable, however, even after a number of analyses, to assign any satisfactory formula to this substance.

It appeared probable that the dinitro-derivitive would be less likely to cause the formation of secondary reactions, and, if this were the case, a dinitrosulphocyanbenzene would be created. It was found on experiment that the reaction did take place easily and in quite quantitative relations.

Dinitrobrombenzene was dissolved in methyl alcohol, and about half its weight of potassium sulphocyanide added. The flask was placed on a water-bath and connected with a return condenser. After boiling a short time the precipitation of a yellow, crystalline sand begins, the amount of which continually increases. To avoid the excessive bumping which soon takes place, it is well, at intervals, to pour off the liquid, remove the sand, and begin the boiling anew. After an hour's boiling but little more precipitation takes place. The sand should then be removed and the liquid distilled down about one-half. On boiling the remaining liquid as before, a fresh deposit of sand will take place. In this manner a very satisfactory yield is obtained. The liquid shows a strong reaction for bromides as soon as this precipitation of the sand begins.

Dinitrosulphocyanbenzene.

The yellow sand obtained by the method just described was well washed with boiling methyl alcohol to remove any traces of the dinitrobrombenzene, and then repeatedly boiled out with water until free from bromides. When dry the substance is a fine sand, which consists of yellow, crystalline, transparent grains. It is moderately soluble in boiling chloroform, which is the best solvent which we have yet been able to find for it. Crystallised from chloroform it forms buff-yellow, small, hard, transparent crystals fusing at 139°.

Analysis:—

$C_6H_3(NO_2)_2SCN$.	Calculated.	I.	II.
C	37.33	37.12	37.43
H	1.33	1.51	1.37
N	18.66	18.24	18.06
S	14.22	14.43	—

* A communication from the Chemical Laboratory of Rutgers College.

† Journ. Prakt Chem: 2, 1, 145.

The substance is reduced with difficulty by tin and hydrochloric acid. The resulting base was not examined. The substance was slowly dissolved by concentrated boiling caustic soda, but no definite compound could be isolated from the resulting solution.

Dinitrophenylmercaptan.

When dinitrosulphocyanbenzene is added to an excess of concentrated sulphuric acid and the mixture gently heated, the reaction begins and the temperature rises, while large amounts of sulphur dioxide and carbon dioxide are evolved, and ammonium sulphate is formed in the solution. The substance, which at first goes into solution in the acid, is re-precipitated. The resulting liquid and precipitate were allowed to cool somewhat and then poured carefully into a sufficient volume of cold water. The precipitate was filtered off and washed with hot water till no reaction for sulphuric acid was obtainable.

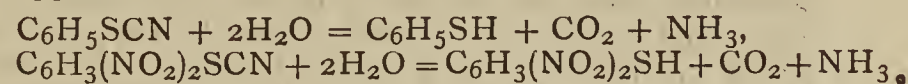
As we were unable to find any solvent for this substance from which we could crystallise it (even nitrobenzene failing to give satisfactory results), we proceeded to purify by repeated extractions with boiling alcohol, and lastly with boiling chloroform. The compound obtained after drying is an impalpable, light yellow powder. It is extremely adherent to glass, which makes it rather difficult to transfer it from one vessel to another, and it is also not easy to obtain it perfectly free from moisture.

$C_6H_3(NO_2)_2SH$. Calculated.

C	36	35.50	35.50
H	2	2.66	2.17
N	14	14.40	—
S	16	15.57	—

The substance is insoluble in the usual solvents. Nitrobenzene dissolves small amounts of it, but we were unable to obtain it again in a crystalline condition. It dissolves easily in warm, concentrated nitric acid, and is precipitated unchanged on pouring the solution into cold water. It fuses at 195°, and on heating it deflagrates.

We were somewhat at a loss at first to understand the reaction taking place here, but on comparing it with the action of concentrated hydrochloric acid under pressure on sulphocyanbenzene,* the mechanism of it was at once apparent.



The evolution of sulphur dioxide is probably due to a secondary action. If the action is continued too long, or the heat is raised too high, the substance is decomposed, and the compound is not obtained.

Dinitrophenylsulphide.

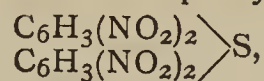
When dinitrosulphocyanbenzene is added to a mixture of fuming nitric acid and concentrated sulphuric acid, and the whole warmed, an energetic action takes place. The resulting solution was poured into water, and the white, flocculent precipitate which separated was washed out with boiling water and dried. It formed a grayish-white mass with a very irregular fracture. It dissolved in boiling glacial acetic acid with some difficulty, but more easily when it was well rubbed with the acid in a mortar so as to remove the adhering film of air. From this solution it crystallised in beautiful transparent, slightly yellow needles nearly a quarter of an inch long and about as thick as a pin, forming fan and stellar aggregates and fusing at 245°.

Analysis gave—

$(C_6H_3(NO_2)_2)_2S$.	Calculated.	Found.
C	39.34	39.20
H	1.64	1.57
N	15.30	15.38
S	8.74	8.82

* Billeter: Ber., vii., 1753.

The substance is then dinitrophenylsulphide—



and is hence isomeric with the one discovered by Beilstein and Kurbatow.*

CORRESPONDENCE.

DIFFERENTIAL RESISTANCE THERMOMETER.

To the Editor of the Chemical News.

SIR,—The sensibility of the instrument described by Mr. Mendenhall in your issue of June 18th (CHEM. NEWS, vol. liii., p. 293) would be more than doubled by stretching two wires from top to bulb of thermometer tube, so that the current passed down one wire, through the mercury to the other wire, and so to the top again. Equation (1) in Mr. Mendenhall's paper would then become—

$$R_t = R_0 - 2st(1 + kt).$$

Such a thermometer in connection with a simple form of Wheatstone bridge may be made to read off the temperature direct by once for all obtaining balances at known temperatures, and so dividing the bridge wire into temperature degrees. Again, a simple form of ohm-meter could be used with its scale divided in the way I have indicated. No adjustments whatever would then be necessary before taking readings; in fact, if the battery were always on, a continuous record could easily be obtained.—I am, &c.,

SYDNEY EVERSLED.

Kenley, Surrey, July 26, 1886.

THE GAS ENGINEERS' CHEMICAL MANUAL.

To the Editor of the Chemical News.

SIR,—In handing you my just-issued book, which bears the above title, I hope you will allow me to make a short statement in your influential journal, the CHEMICAL NEWS.

My book consists of seven chapters. Chapter I., the Introductory, shows the great extent of the Gas Industry in this country, viz., that about £70,000,000 is embarked in it as its capital, and gives a sketch of the operations performed in gasworks. Chapter II. is on Coal. Chapter III. is devoted to Gas. At the end of the chapters there is a short table of the weights of 100 cubic feet of some of the commonest gases. The table has been calculated by myself, and is, I believe, more accurate than any other table of these weights which has hitherto been published. The same chapter contains an account of my system of gas-analysis, which, according to the remark in the preface, "has claims to be considered as being, in some subordinate sense, new and original."

Tar, Gas-liquor, Coke, and lastly, Purification of Gas, have each of them a chapter specially assigned to them.

Faults and omissions the book has—the author will doubtless hear of them in due time from his readers and his reviewers.—I am, &c.,

J. ALFRED WANKLYN.

July 27, 1886.

On a Crystalline Potassium Alcoholate.—R. Engel.—The author has obtained a compound which he names potassium alcoholate. The same name has been applied to compounds of alcohols and bases in which the metal is substituted for the hydrogen of the alcohol. To avoid confusion he therefore proposes to reserve for these latter bodies the names of methylates, ethylates, &c.—*Comptes Rendus*, vol. ciii., No. 2.

* *Ann. d. chem. u. Pharm.* 197, 77.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 2, July 12, 1886.

Identity of Origin of the Fluorescence $Z\beta$ on Reversal and of the Bands obtained in a Vacuum.—Lecoq de Boisbaudran.

Formation-Heat of Hydroselenic Acid.—Ch. Farre.—The formation-heat of gaseous hydroselenic acid, setting out from gaseous hydrogen and amorphous selenium, is -9.44 cal.

New Species of Asparagine.—A. Piutti.—The rotatory power of this new asparagine is equal to that of the normal variety, but of an opposite sign. The chemical properties of the two compounds and of their respective derivatives are identical.

Division of a Base between Two Acids: Particular Case of Alkaline Chromates.—P. Sabatier.—Chromic acid behaves with the alkaline bases like a bi-basic acid having two distinct functions. As regards potassa the first function of chromic acid, that which yields bichromate, is surpassed only by the first function of sulphuric acid, which yields potassium bichromate. It is very near that of hydrochloric acid, and is certainly superior to the carbonic, acetic, and even phosphoric acids. Hence potassium bichromate undergoes no notable decomposition except with sulphuric acid, which, moreover, does not occasion any change of colour in the liquid. Potassium bichromate, which retains the second function of the chromic acid and forms neutral chromate, ranks below hydrochloric acid, potassium bisulphate, acetic acid, and the first function of phosphoric and carbonic acids. But it appears to be an acid stronger than potassium bicarbonate and the third function of phosphoric acid. The action of powerful acids upon neutral potassium chromate tends to the total displacement of the bichromate in favour of the new acid.

Crystalline Barium and Strontium Titanates.—L. Bourgeois.—The author has studied the crystalline earthy alkaline titanates by fusing the elements of the salt in the corresponding chloride. The crystals of the barium compound have the sp. gr. 5.91, and their composition is $2\text{BaO}, 3\text{TiO}_2$. The strontium compound has the sp. gr. 5.1, and its composition is similar to the foregoing. The calcium compound is identical with perovskite, CaO, TiO_2 .

Action of Chlorine upon Potassium Selenocyanide.—A. Verneuil.—The action of chlorine upon the alkaline selenocyanides is quite different from that which it exerts upon the corresponding sulphocyanides.

Transformation of the Glucoses into Dextrines.—E. Grimaux and L. Lefèvre.—The authors effect this transformation by means of dilute hydrochloric acid. The dextrine obtained belongs to the group of the achro-dextrines and is not coloured by iodine. The dextrines which have been isolated by various chemists (achro-dextrines α , β , &c.) cannot be regarded as distinct chemical species, but as mixtures which it is not possible to separate.

Electrolysis of an Ammoniacal Solution with Electrodes of Carbon.—A. Millot.—This paper will be inserted in full.

On Propionic acid.—Ad. Renard.—Propionic acid occurs in considerable proportions in the tars resulting from the destructive distillation of resin at the temperature of bright redness. Propionic acid boils at 141.5° to 142° . Its sp. gr. at $0^\circ = 1.0089$; at $+18^\circ = 0.9904$. It remains liquid if cooled to -50° . It dissolves in all pro-

portions in water, alcohol, ether, benzol, and petroleum essences.

Conversion of Amides into Amines.—H. Baubigny.—The author described the transformation of amides into amines (by heating with an alcohol in a closed vessel) in a sealed paper deposited with the Academy in 1880, opened in 1882, and published the same year in the *Comptes Rendus* (vol. xcv., p. 646). He expresses his surprise that R. Seifert should have published this conversion as a new reaction (*Berichte Deutsch. Chem. Gesellsch.*, xviii., p. 1355).

Isomerism of the Camphols and Camphors.—Alb. Haller.—On comparing the properties of valerianic camphol and its derivatives with those of the camphol of N'gai and its corresponding derivatives we conclude that the two products are completely identical. Their camphor is also identical with that of mother-wort (*Matricaria*).

Researches on the Development of the Sugar-Beet.—Aimé Girard.—Not suitable for abstraction.

Moniteur Scientifique, Quesneville.
3rd Series, Vol. xvi., July, 1886.

Manufacture of Toilet Soaps.—Dr. C. R. Alder Wright.—From the *Journal of the Society of Arts*.

Manufacture of Leather in Russia.—M. Ryloff.—From this extensive paper it appears that the matters chiefly used in tanning are the bark of the oak containing from 6.04 to 4.37 per cent of tannin according to the season, that of willows, of the elm, and the birch. The leaves of the arbutus, employed in the governments of Kasan, Viatka, and Perm, contain about 16 per cent of tannin, while the root of wild sorrel (*Rumex acetosella*) contains 12 per cent. For removing the hair from hides a lye made from wood-ashes is still employed. The softening of the leather is effected by means of the excrement of dogs, which acts on the leather by means of the biliary acid present, which forms with soda a kind of soap. After tanning white Russia leather is coated with a mixture of tar and of seal oil. Black Russia leather is dyed with alum, extract of sanders, and ferrous sulphate. Horse-hides are tanned to a great extent for sole-leather.

Analysis of Fertilising Matters known as Commercial Manures.—Report of the Second Annual Meeting of Official Agricultural Chemists at Washington. Translated from CHEMICAL NEWS.

Memoir on the Molecular Volumes of Liquids (being a Critique on a Memoir by MM. Bartoli and Stracciati, published in the *Annales de Chimie et de Physique*, March, 1886).—Hermann Kopp.—This memoir is, from its nature and extent, insusceptible of useful abstraction. A preliminary correspondence is appended explaining why it has not been published in the *Annales de Chimie et de Physique*.

Properties and Proprietors of Ungreenable Aniline Black.—This correspondence consists of a reply to M. Grawitz by M. Camille Kœchlin and of a letter on the same side by D. d'Andiran Kœchlin.

Salicylic Acid.—The brewers of Central and Southern France are protesting against the prohibition of the use of salicylic acid as preservative of beer, which, they urge, places them at a disadvantage as compared with their foreign rivals.

Artificial Colouring-Matters applied in Industry.—Dr. E. Noëlting.—In this sixth and last lecture Dr. Noëlting reviews the safranines, the indophenols, the indulines, methylene blue, &c.

Industrial Society of Mulhouse.—Session of the Chemical Committee, May 12, 1886.

M. Bourcart remarked that he had repeatedly tried the method of Lux (*Moniteur Scientifique*, Jan., 1886) for detecting small quantities of fatty oils in mineral oils, and that it had given excellent results. The method consists

in heating the oil in question with a little sodium or caustic soda. If it contains 1 to 2 per cent of fatty oil it thickens and becomes gelatinous on cooling. A pure mineral oil similarly treated remains unaltered.

M. Camille Kœchlin proposes three new prizes, the last taking the place of No. VII., which has been withdrawn.

1. Medal of honour for a process for preparing cotton with albumen without rendering it harsh. This preparation is to serve as a mordant for dyes which cannot be fixed by means of metallic preparations.

The similarity of the tinctorial properties of wool and of albumen seems to render the solution of this important problem practicable.

2. Medal of honour for a steam albumen orange, of the tone, the intensity, and the fastness of orange minium, easy to print, and not affected by steaming.

3. Medal of honour for an investigation of the colouring-matters fixed respectively by: *a*, the intervention of metallic mordants; *b*, by fatty mordants; *c*, by means of other colouring-matters; and *d*, those which dye without any intermediary.

The Assay of Quinine.—Dr. J. E. de Vry.—From the *Chemist and Druggist*.

On Quinine Hydrate.—Dr. O. Hesse.—From the *Pharmaceutical Journal*.

Kolbe's Synthesis of Salicylic Acid.—R. Schmitt.—From the *Journal für Praktische Chemie*.

Coloured Reactions of the Phenols with the Carbohydrates.—Anton Ihl.—From the CHEMICAL NEWS.

Determination of Ferric Oxide and Alumina in Phosphates.—Bernard Dyer.—From the CHEMICAL NEWS.

Determination of Glycerin.—W. Fox and J. A. Wanklyn.—From the CHEMICAL NEWS.

Glucose and the Glucasic Saccharification of Amylaceous Matters.—Leon Cuisinier.—The author admits the pre-existence of the glucogenous ferment or *glucose* in grains before germination, as also the production of a liquefying diastase, *maltase*, by germination.

Chemical Patents obtained in France.—A list of the titles of patents for February.

Bulletin de la Société Chimique de Paris.
Vol. xlv., No. 1, July 5, 1886.

Certain Approximations between Chemistry and Physics.—A. Colson.—The author concludes that for isomers of position the product of the density by the specific heat is constant. Further, isomeric bodies possess the same coefficient of expansion under a constant pressure. From these two propositions there follows a consequence. M. J. Moutier has established that for bodies possessing the same coefficient of expansion under a constant pressure and at a constant volume the product of the specific heat by the density will be constant. By applying this proposition reciprocally we conclude that isomers of position possess the same coefficient of expansion at a constant volume. On studying the relation between the physical constants and the formation-heat, the author finds that of two isomers of position the more dense is formed with the greater quantity of heat. As the product of the specific heat by the density is the same for two isomers, it results that the compound whose specific heat is the smaller is formed with the greater quantity of heat. These propositions are not sufficient to enable us to calculate the difference between the formation-heat of two isomers of position. Such, indeed, is not the object in view. The author wishes to sketch a rational plan which the experimentalist may follow in the preparation of isomers. The quantity of heat liberated being an approximate measure of chemical affinity, and the mass reacting being identical, then if one and the same reaction produces several isomers the maximum effect will be

produced by the most intense affinity. In this case affinity seems to act upon the yield as in hydraulics the difference of level acts upon the flow.

Biedermann's Central Blatt fur Agrikultur Chemie.
Vol. xv., Part 3.

Preservation of Farm-Yard Manure.—Prof. Holdefleiss.—A former result is confirmed, *i.e.*, that manure prepared with potash salts acts less rapidly than that preserved with earth but retains its efficacy longer. The proportion of starch in potatoes is, however, reduced by the former.

Action of Kainit as a Manure at Walna.—Pirscher.—Not only moorlands but sour humous sandy soils can be made to yield remunerative crops by treatment with kainit.

Manurial Experiments with Phosphates in the District of Hanover.—F. Brüggmann.—A mixture of Gilchrist and Thomas slag with kainite was found to be the most remunerative application.

Manurial Experiments on Potatoes.—Schrewe.—The application of large quantities of soda-salt-petre with and without phosphates proved remunerative.

Feeding Experiments on Sheep with Raw Sugar.—Prof. Werner.—The author finds that neither raw sugar nor sugar-beets give as good results as bruised corn and mangolds.

Feeding Experiments on Cows with Reference to the Yield of Milk.—Dried brewer's grains were found equal in effect to rape cake, earth-nut meal, &c.

Researches on the Transformation of Matter in Swine.—F. Strohmer, Dr. N. v. Lorenz, and Dr. E. Meissl.—This paper does not admit of useful abstraction.

Cultivation of Grain on the Experimental Field at Grignon in 1884.—P. P. Dehérain.—Already noticed.

Cultivation Experiments with Swedish Grain.—Prof. Leydhecker, A. Müller, and G. Duchman.—Experiments undertaken apparently with a view to ascertain the use of seeds from a more severe climate.

Nutritive Value of Different Portions of the Grain of Wheat.—Aimé Girard.—The author shows that the advantage derived from grinding up the entire grain must be very small, as by far the largest portion, both of the nitrogen and of the mineral matters now rejected, are not capable of digestion and assimilation.

Non-crystalline Products of the Action of Diastase upon Starch.—H. T. Brown and Dr. G. H. Morris.—From *Liebig's Annalen*.

Application of Electricity in the Sugar Manufacture.—Prof. H. Landolt, Dudok de Wit, J. Görz, and others.—No results of importance have been reached. There is a complaint against the morbid desire to effect everything by electricity.

Journal de Pharmacie et de Chemie.
Series 6, Vol. xiii., No. 11, June 1, 1886.

Determination of Organic Carbon contained in Soils which Fix Free Nitrogen.—M. Berthelot.—Already noticed.

Chemical Characteristics of the Different Kinds of Digitaline.—M. Lafon.—The digitaline of French make is identical with the digitoxine of Merck, of Darmstadt.

Note on the Pichi of Chili.—L. Limousin.—A pharmaceutical paper.

Determination of Acid Magenta in Wine.—M. Sambuc.—Already noticed.

Coal-Tar Colours from a Sanitary Point of View.—P. Cazeneuve.—The author considers that the addition to wine of colouring-matters, whatever they may be, ought to be energetically proscribed.

Oxidation of the Fatty Acids.—H. Carette.—The author considers that the lipic acid of earlier authors is probably identical with normal propylene dicarbonic acid.

No. 12, June 15, 1886.

On Ephestia Kuenhilla.—An account of a newly introduced moth which infests granaries.

A New Note on Acid Magenta in Wines.—P. Cazeneuve.—A reply to the memoir of M. Sambuc in the last number of the *Journal de Pharmacie et de Chimie*.

Researches on the Physiological Action of Urethane and on its Properties as a Functional Antagonist of Strychnine.—Prof. Coze.—Urethane has a manifest hypnotic action; it slackens the pulse and the respiration and lowers the temperature. It is the functional antagonist of strychnia and might be useful in tetanus.

MISCELLANEOUS.

Appointment.—Mr. H. Lloyd Snape, B.Sc., formerly Demonstrator of Chemistry at University College, Liverpool, has been appointed Lecturer on Chemistry and Chemical Technology at the Manchester Technical School.

Manchester Technical School.—On Friday evening (July 23) the students attending the Manchester Technical School assembled in strong force in one of the lower rooms of the Institute, and presented an illuminated address, a microscopic slide cabinet, and half-a-dozen volumes of Professors Roscoe and Schorlemmer's Treatises on Chemistry and Spectrum Analysis to Dr. A. B. Griffiths, F.R.S. (Edin.), F.C.S. (Lond. and Paris), as a mark of esteem and respect and affectionate regret at his departure from the school, where he has laboured as a lecturer and scientist with marked success. The chair was occupied by Mr. Harold Follows, F.C.S., and the presentation was made by Mr. Asher-Aron. Dr. Griffiths acknowledged the gifts, and then spoke of the importance of original research as a means of enlarging the mind, pushing forward the bounds of knowledge, and also for the good of humanity. The address speaks of Dr. Griffiths's "masterly and vigorous discourses," to the "honour he has conferred upon the School by his brilliant and ingenious researches," and to "the warmth and cordiality with which Dr. Griffiths has at all times met the demands of individual students," and also to "the hearty and inspiring personal sympathy with which he has so uniformly tendered his invaluable advice and assistance." The cabinet mentioned as one of the gifts is capable of holding 500 slides. It contains a large number of biological and pathological slides, and is also inscribed with a silver plate. Dr. Griffiths has recently been appointed Head Master and Lecturer on Chemistry and Physiology at the new School of Science of the City and County of Lincoln.

Etched Figures and Arrangement of Atoms.—W. S. B.—The method of "etched figures," which within the past few years has proved so successful in the detection of hemihedral and tetartohedral forms on crystals which appear to be holohedral, bids fair to play some part in the discussion regarding the position of the atoms in the molecules of crystalline substances. When Linnæite (Co_3S_4) is treated with acids its cubic faces are most readily attacked. When treated with fused potash, however, the solution takes place most rapidly in the direction of the dodecahedral planes. This fact leads F. Becke (Tschermak's "Min. und Petrogr. Mitt." 8, 195) to observe that probably the cobalt atoms in the molecule are turned towards the cubic faces and the sulphur atoms towards the dodecahedral faces. Whether the use of this method will throw any light on the position of the atoms in space is doubtful. It is probable, however, that it will help to an understanding of the forces which act in the formation of crystals.—*American Chemical Journal*.

THE CHEMICAL NEWS.

VOL. LIV. No. 1393.

ON RADIANT MATTER SPECTROSCOPY.*

PART II.—SAMARIUM.

By WILLIAM CROOKES, F.R.S.

(Continued from p. 57).

Mixed Samarium and Yttrium Spectra.

146. It was interesting to ascertain what spectrum a mixture of samarium and yttrium would give. A mixture of 90 parts of samaria to 10 of yttria was treated with sulphuric acid and then ignited, and afterwards examined in the radiant-matter tube. The result was as remarkable as it was unexpected. Scarcely a trace of the yttrium spectrum could be detected. The powder phosphoresced with moderate intensity, but the spectrum was almost the facsimile of that given by pure samaric sulphate (137, Fig. 3), except that the sharp orange line, which in the spectrum of pure samaric sulphate is only just visible, had gained sufficiently in intensity to be measurable, and was found to lie at 2693. I next tried a mixture of samaria 80, and yttria 20. The spectrum was identical with the one last observed, with one striking difference—the 2693 line now shines out with great brilliancy of a fine orange-red colour, as sharp as a gas line, and so unlike the bands usually met with in the spectra of phosphorescent earths as to suggest the explanation that some other spectrum-forming body was present in the mixture.

The next tube experimented with contained 70 parts of samaria and 30 parts of yttria. The spectrum was identical with the one last observed. The sharp orange line was present in full intensity.

147. Mixtures were now made of samaria 60, yttria 40; samaria 60.63, yttria 39.37 (equivalent proportions of the two earths); in this last a slight division could be detected in the green band. The following experiments were continued; mixtures were prepared in the following proportions:—

Samaria.	Yttria.
58	42
56	44
54	46
53	47
52	48
51	49
50	50
49	51
48	52
47	53
46	54
45	55

The results were almost identical with those yielded by the previous mixtures. The green band gradually condensed into two bands at $\frac{1}{\lambda^2}$ 3133 and 3199 as the proportion of yttria increased; the first green band was stronger than the other, and the wide orange band began to show signs of a wing on the side next the green. At this stage the spectrum nearly resembled the lead-samarium spectrum (145, Fig. 6). Very little of the yttria spectrum could be detected, and the brilliant orange line stood out sharply in the whole series.

In the next mixture—samaria 44, yttria 56—a faint band ($\frac{1}{\lambda^2}$ 3038) was visible by the side of the two green

bands, in the position occupied by the yellow band of yttria.

148. The experiments were continued, and the following mixtures were made and carefully mapped:—

Samaria.	Yttria.
43	57
42	58
41	59
40	60
39	61

The faint line first observed in samaria 44, yttria 56, gradually got stronger, and there were also signs of a double green band in about the position occupied by the yttrium green.

149. The change which had been rapidly coming over the spectra since samaria 43, yttria 57, was now nearly accomplished, and in the next trial mixture—samaria 35, yttria 65—the only indication that could now be found of the samarium spectrum was seen in the two faint green bands next to the citron line of yttria, a faint yellow band, and the new orange line, which shone out as brightly and sharply as ever.

The series was continued:—

Samaria.	Yttria.
30	70
25	75
20	80
10	90
5	95

In each case a careful map of the spectrum was taken on the $\frac{1}{\lambda^2}$ scale, and each spectrum was found to be

practically identical. Slight differences in the relative intensities of some of the bands were observed; but the general character of the spectrum was unaltered. The yttria spectrum now shone forth with scarcely any band of samaria, except that, standing out beyond the other bands in sharpness and brilliancy, the 2693 line was present in all.

150. It will be remarked that a sudden change occurs between the two mixtures, samaria 45, yttria 55, and samaria 35, yttria 65; on one side the spectrum pertains to that of samaria, whilst on the other side the spectrum is that of yttria, the new orange line running equally across them all.

151. The diagrams of some of these intermediate spectra shown in the accompanying figures illustrate how sudden is the transformation from the samarium to the yttrium spectrum. Fig. 7 is the spectrum of a mixture of 44 parts samaria and 56 parts yttria, and except for the increased strength of the orange line, and a faint trace of the red and yellow yttria bands, it is the pure samarium spectrum. Fig. 8 is the spectrum of 42 samaria and 58 yttria, and is built up of some of the component bands of the spectrum of each earth; whilst in Fig. 9, the spectrum of 39 samaria and 61 yttria is seen to be almost the yttria spectrum.

152. I have already shown (86) that one part of yttrium can be detected spectroscopically in the presence of a million parts of calcium, and the reaction is almost as sensitive if other earths are taken instead of lime. Again, the spectrum test for samarium is, if possible, even more delicate (156 to 163), one part being detectable when mixed with more than two million parts of calcium.

153. The accompanying diagram (Fig. 10) shows at a glance the remarkable effect these two earths have of masking each other's spectrum reactions. The ordinates above the horizontal zero line represent the percentages of samaria in the mixtures examined, and the lower ordinates show the percentages of yttria present. The dots on the horizontal line show the actual mixtures experimented with (146 to 149). The part to the left covers the mixtures showing a preponderance of the samarium

* A Paper read before the Royal Society, June 18, 1885.

FIG. 7.

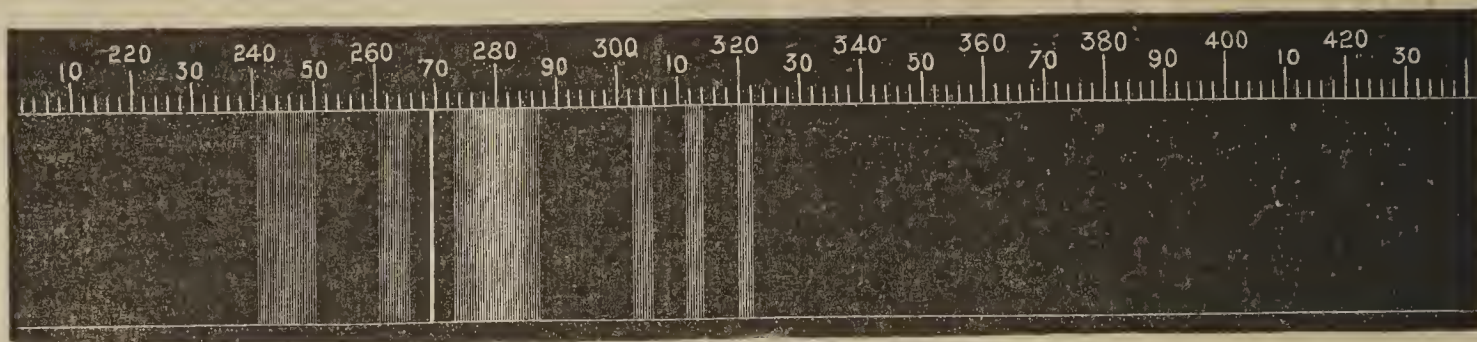


FIG. 8.

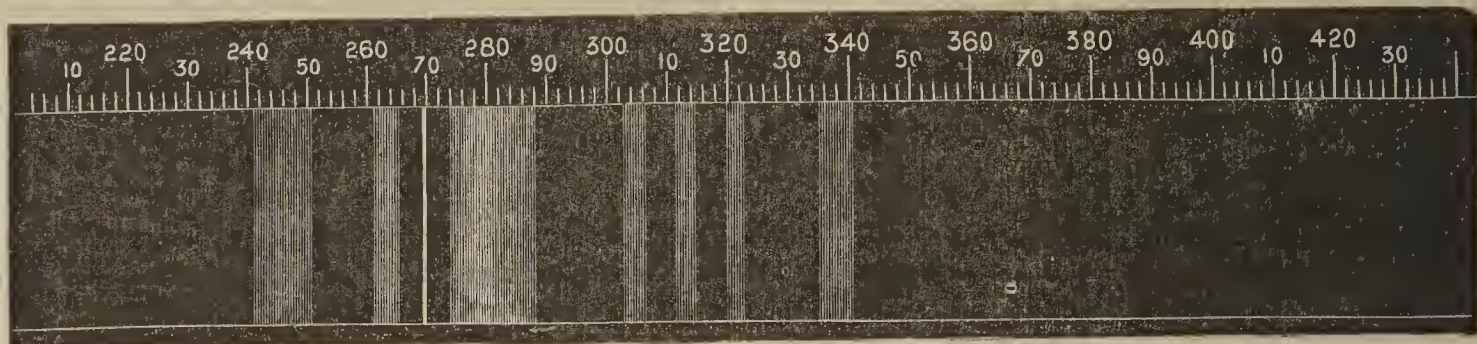


FIG. 9.

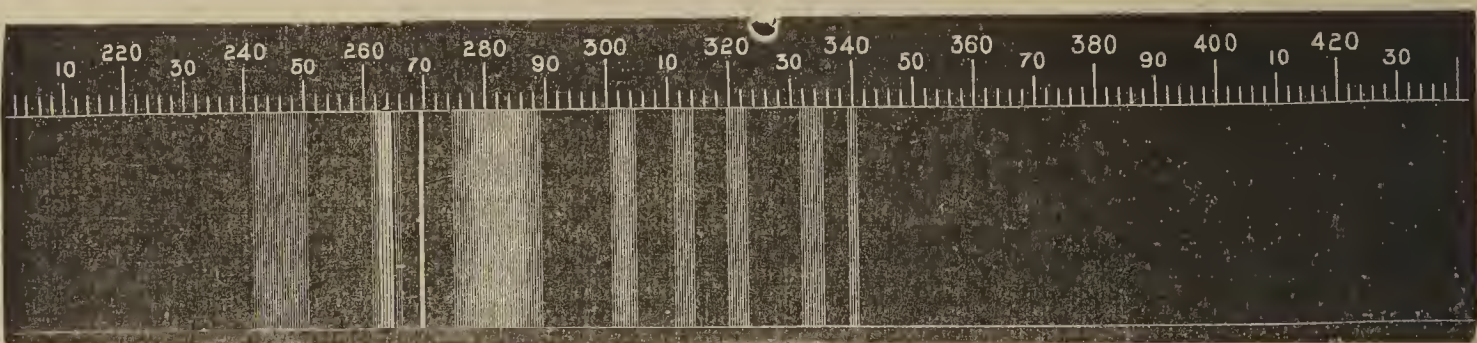


FIG. 10.

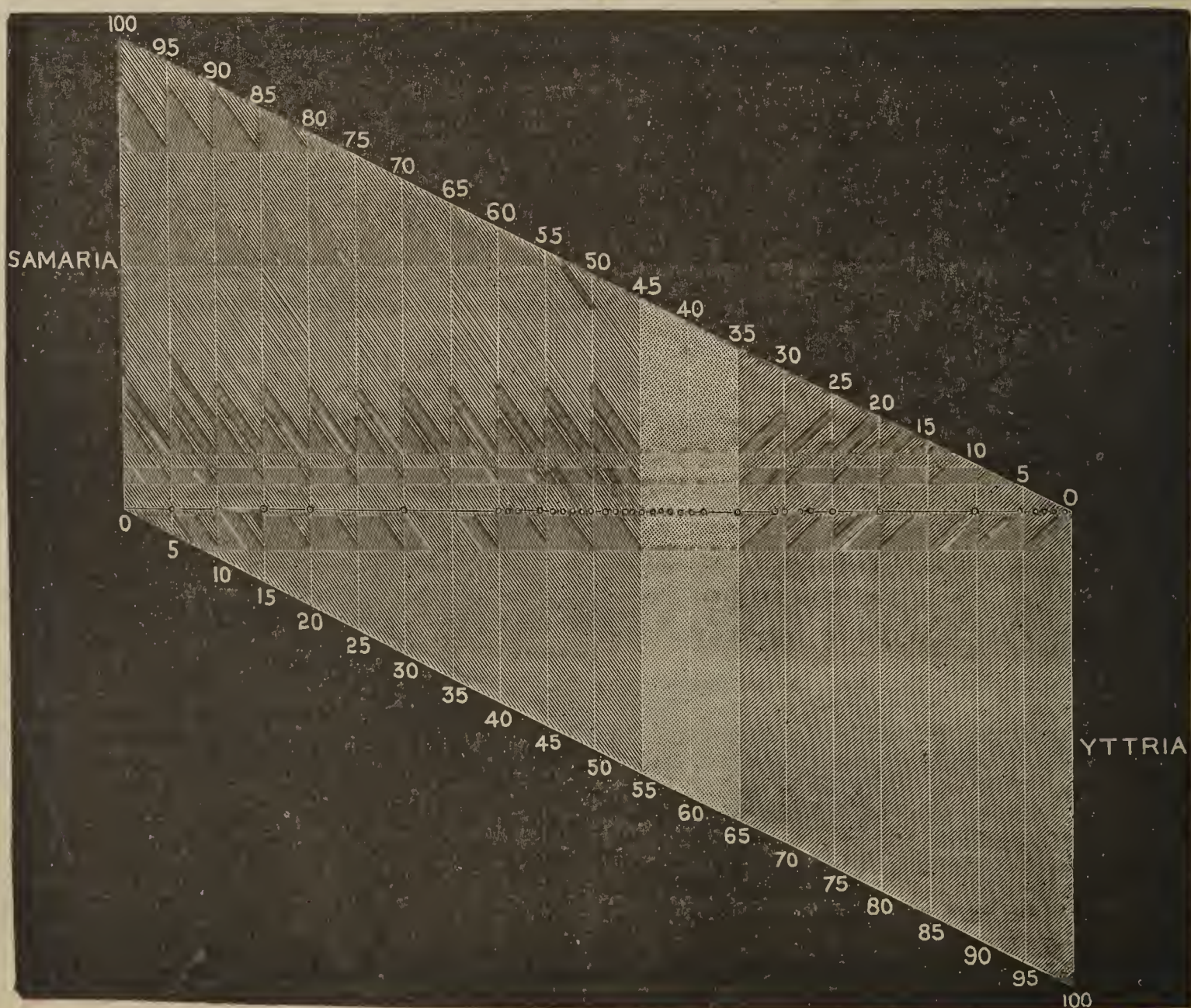
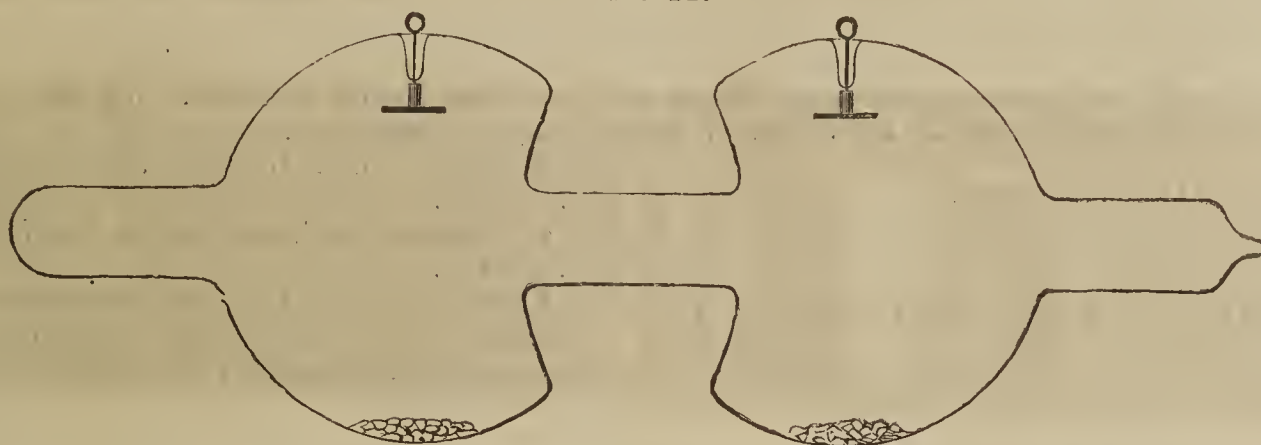


FIG. II.



spectrum, and the right-hand portion shows the mixtures which give preponderance to the yttrium spectrum only. The intermediate portion covers the narrow border-land in which the fainter mixed spectra were observed.

In no mixture does the resulting spectrum contain the complete spectrum of either earth, many bands of each being suppressed.

154. It was of interest to ascertain whether the orange line 2693 could be evoked by mechanically forming a mixture which, when prepared chemically, gave the line strongly.

A radiant-matter tube was made in the form of a double bulb, as shown in Fig. II.

posed, and had no resemblance to the spectrum shown by a similar mixture prepared by solution and chemical action (Fig. 13).

The Action of Calcium on the Samarium-Yttrium Spectrum.

155. The addition of calcium to mixtures of samarium and yttrium has the effect of greatly developing the samarium spectrum, and, *pari passu*, of impairing the sharpness of the bands of the yttria spectrum. This exaltation of the samarium bands is not, however, effected without a corresponding loss. The brilliantly sharp orange line 2693 entirely disappears.

FIG. 12.

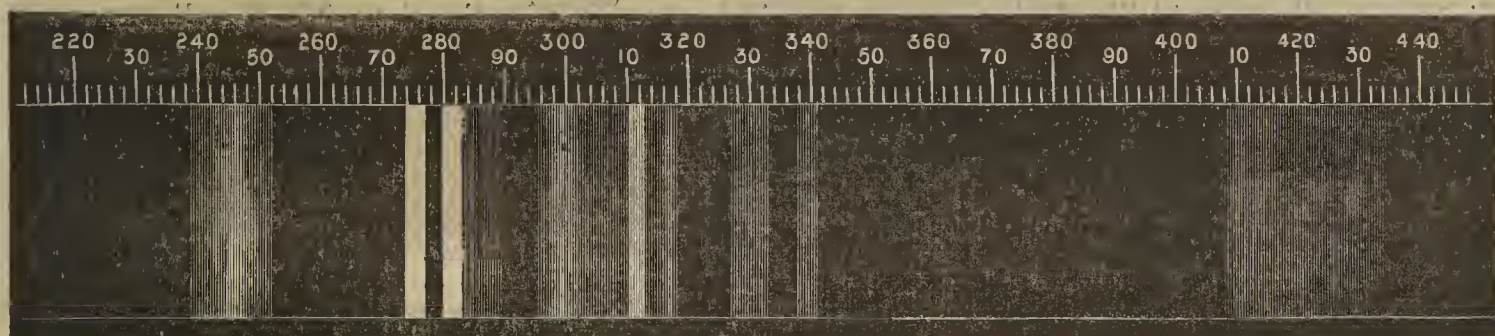


FIG. 13.

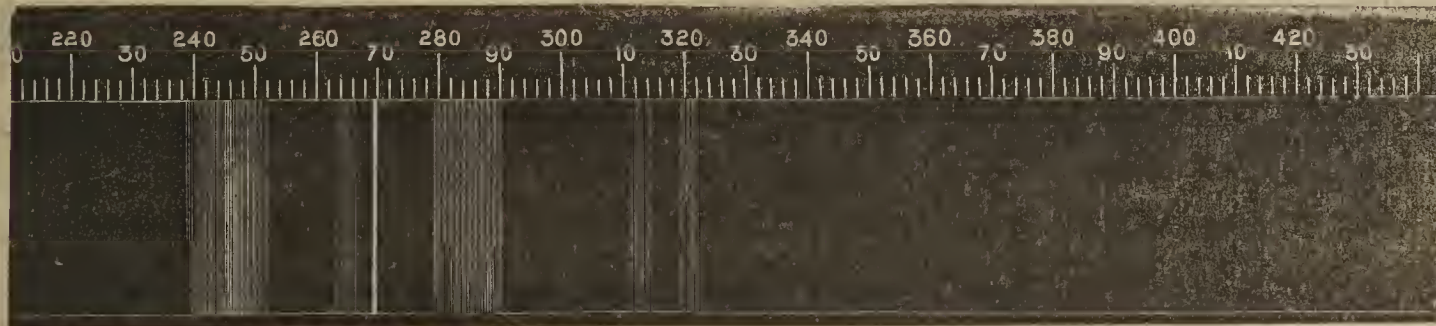
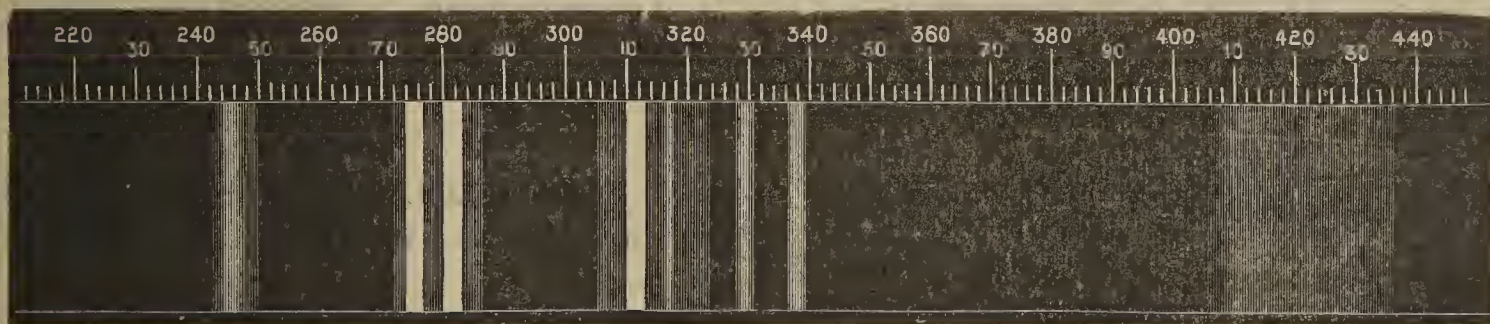


FIG. 14.



In one half was introduced ignited samaric sulphate, and in the other half the same weight of yttric sulphate, each being finely powdered. The tube was well exhausted, and the powders separately examined with the spectroscop. Each gave its characteristic spectrum (72, 137). The double bulb was now sealed off, and the powders well mixed by violent agitation. On careful examination it was seen that the spectrum shown by the mixture was simply that of the two components super-

Fig. 12 is a drawing of the spectrum given by a mixture of equal parts of samaria, yttria, and lime. On comparing it with Fig. 13, which represents the spectrum given by the same mixture without the lime, it will be seen that the action is as might have been anticipated from previous experiments. The lime has divided the samarium orange band and strengthened the red, whilst it has increased the brilliancy of the yttrium citron and green, and brought out the blue and violet bands.

Fig. 14 is a representation of the spectrum given by a mixture of samaria 2, yttria 54, and lime 44. Even with this large amount of yttria present the samarium spectrum greatly overpowers that of yttrium. Without the lime very little samarium would be visible in this mixture (149).

(To be continued).

VERIFICATION OF THE CALCULATION OF THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 53.)

On the Materials employed in the Experiments.

SILVER has been the standard in all these researches, since no other body has ever been obtained in such a pure state. M. Stas considers that distilled silver is the purest possible, and has served as the standard of comparison for silver from other sources. This comparison is made by the wet method; different titrations of the same silver agree within 1-100,000th.

Since Dumas's discovery[†] that silver melted with nitre can retain as much as 25-100,000ths of its weight of oxygen, many chemists have been led to consider M. Stas's silver to be contaminated with this impurity. I cannot share these doubts so long as it is not disproved that the titration of M. Stas's own silver or of silver prepared *exactly* according to his instructions increases by heating to 600° *in vacuo*.

The chlorides and bromides of potassium and sodium always contained a few 1-100,000ths of silica, which was accurately weighed by subliming these salts in a current of nitrogen. I have admitted that this anhydrous silica was simply mixed with the chlorides. It is, however, not impossible that the silica might exist, at least partially, as an alkaline salt. In this last supposition the correction will become greater in the case of the relation between silver and the chlorides or bromides, and less for that between the chlorides and nitrates.

The calculations of relationships between simple and compound bodies, such as that of atomic and molecular weights, are always founded on the *actual* weights of the substances employed. The reduction *in vacuo* is indispensable, but save a few evident errors I have throughout taken the figures as I find them in the memoirs, inasmuch as M. Stas[‡] has but rarely given the specific weight which he takes, and the weight of a litre of air at the moment of weighing.

In the following tables I have marked with an asterisk the weights (in grms.), the proportions, and the atomic weights, which differ sensibly from those found in the

* *Ann. Chim. Phys.*, 6th Series, vol. vii., April, 1886.

† It is not easy to understand how this can be possible with a pipette whose drops had a variation of 4-100,000ths. I cannot imagine why M. Stas measured his saline solution instead of weighing it, as Gay-Lussac ("Instruction," p. 11) advised, for researches requiring great accuracy.

‡ *Annales de Chimie et de Physique*, 1878, vol. xiv., p. 294. M. Marignac suspected this cause of error; *Archives des Sciences Physique et Naturelles*, 1860, vol. ix., p. 104. In any case we gain nothing by Prout's theory as M. Stas has explained (*Bulletin de l'Académie de Belgique*, 1880, vol. i., p. 417).

|| I only recall the following points which concern these specific weights determined by M. Stas:—

NaCl = 2.125 to 2.150 (α 274).
NaCl = 2.145 (β 41).
NH₄Br = 2.456 (γ 45).

then M. Stas has admitted:—

According to M. de Marignac, AgNO₃ melted = 5.38.
" " Pierre, Br " = 3.187.
" " Troost, LiNO₃ " = 2.442.
" " Kresners, NaBr " = 3.079.

In several places, for example (γ 75) we find indicated how much a body, weighed in air with platinum weights, loses per grm. more than these latter. But in going over these calculations I noticed that M. Stas does not always use the same density for air.

Memoirs. The maximum and the minimum of a table are shown by M and m. The letters α , β , γ , followed by a number, indicates the memoir and the page.

α . *Bulletin de l'Académie de Belgique*, August, 1860, vol. x., p. 208—336.

β . *Memoirs de l'Académie de Belgique*, 1865, vol. xxxv., p. 1—311.

γ . *Memoirs de l'Académie de Belgique*, 1882, vol. xliii., p. 1—103.

I have considered the most reliable proportion to be the arithmetical mean of all the determinations of the same kind, except in such cases when M. Stas himself has shown reasons for excluding any of them.

I. Synthesis of Sulphide of Silver, α 225.

Silver.	Sulphide of Silver.	Ag ₂ : Ag ₂ S = 100.
59.4225 grms.	68.24823 grms.	114.8525*
104.139 "	119.6078 "	114.8540*
191.9094 "	220.4158 "	114.8541 M
150.000 "	172.2765 "	114.8510
249.076 "	286.061 "	114.8489 m

Average 114.8521
Log. = 2.0601389

II. Analysis of Sulphate of Silver, α 327.

Sulphate of Silver.	Silver.	Ag ₂ SO ₄ : Ag ₂ = 100.
72.137 grms.	49.919 grms.	69.2003
60.251 "	41.692 "	69.1972 m
81.023 "	56.071 "	69.2038
83.115 "	57.523 "	69.2089 M
55.716 "	38.5595 "	69.2072
63.922 "	44.2355 "	69.2023

Average 69.2033
Log. = 1.8401268

III. Synthesis of Chloride of Silver, α 247.

Silver.	Chloride of Silver.	Ag : AgCl = 100.
91.462 grms.	121.4993 grms.	132.8413 m
69.86735 "	92.8145 "	132.8438*
101.519 "	134.861 "	132.8431
108.549 "	144.207 "	132.8497* M
399.651 "	530.920 "	132.8459
99.9925 "	132.8382 "	132.8482
98.3140 "	130.602 "	132.8417

Average 132.8448
Log. = 2.1233446

As in the sixth estimation an augmentation of weight was impossible, M. Stas considered the following relationship to be more exact.

Log. = 2.1233616 132.850.

(To be continued).

ELECTROLYSIS OF AN AMMONIACAL SOLUTION WITH COKE ELECTRODES.

By A. MILLOT.

In a memoir presented to the Academy, August 17th, 1885, the author announced that on electrolysing retort-coke purified with chlorine with a solution of ammonia containing 50 per cent of liquid ammonia, he obtained a black liquid, and that this liquid if evaporated in the water-bath left a residue composed chiefly of azulmic matters. This residue, if exhausted with alcohol in a cohobator yields a yellow alcoholic solution, and the black matter remains insoluble. In the former paper he mentioned that the alcoholic liquid, evaporated to

dryness, leaves a residue soluble in boiling water but insoluble in cold water, and that after a great number of successive evaporations and of resolutions to separate the matter insoluble in the cold there remained a syrupy liquid in which appeared a crystallisation of urea capable of being separated by draining and successive crystallisations.

He has subsequently found that the alcoholic solution contains not merely urea, but the derivations of that substance which are generally obtained by the action of heat upon urea, such as ammelide, biuret, and guanidine.

To isolate these bodies the alcoholic solution derived from the exhaustion of the black matter, which is always slightly acid, is treated with basic lead acetate after saturation with ammonia. There is formed an abundant precipitate of ammelide. The filtrate is then decomposed with sulphuretted hydrogen and evaporated to the consistence of syrup. A strong hot alcoholic solution of oxalic acid is added, and on cooling there appears a crystallisation of urea oxalate, which is washed with alcohol and is then decomposed in a boiling solution with calcium carbonate. The pure urea is then allowed to crystallise. The solution from which the urea has been separated is treated at a boil with chalk and then with lime-water. It is filtered and the excess of lime is removed by means of ammonium carbonate. The liquid obtained then contains biuret and guanidine nitrate. The nitric acid is derived from the electrolysis of the ammonia, but it is not generated in sufficient quantity to form urea nitrate, since urea may be obtained directly by crystallisation from the crude alcoholic solution. Biuret is separated from guanidine nitrate by crystallisation in a dilute liquid. Biuret being the less soluble crystallises first in the form of warts. These warts, re-dissolved, yield biuret absolutely pure, which crystallises in needles after several re-crystallisations from dilute ammonia and alcohol. The mother-liquor after concentrating deposits an abundant crystallisation of guanidine nitrate, which is purified by successive crystallisations in water and alcohol. It forms hexagonal tables, of which three edges are often suppressed, yielding crystals in the form of triangles. The biuret and the guanidine nitrate thus obtained have exactly the known properties and the percentage composition of these bodies. As for the yellowish-white matter separated in the first place on the evaporation of the alcoholic solution, or on the precipitation with basic lead acetate, it is purified by several dissolutions in heat and precipitations in cold. A little matter which has become insoluble (probably by polymerisation) is separated each time and the boiling solution is treated with basic lead acetate. It is filtered and the liquid is decomposed in heat with sulphuretted hydrogen. The concentrated liquid deposits on cooling a white matter, which when dried gave on analysis the composition and the properties of ammelide (melanuric acid of Gerhardt). The silver salt has the percentage composition of silver ammelidate.

We obtain, therefore, in this electrolysis, by the direct action of coke upon ammonia, an azulmic matter the oxidation-products of which the author is studying; urea and its decomposition-products, ammelide, biuret, and guanidine. The urea and the guanidine spring probably from the actions of nascent carbonic acid upon ammonia with elimination of water. Biuret is probably formed by the reaction of carbonic acid upon guanidine, and ammelide from the action of carbonic acid and urea upon biuret. The author has not observed among these products the formation of cyanuric acid. It ought to be formed by the action of carbonic acid upon biuret, probably in consequence of the presence of ammonia, which under these conditions gives rise to ammelide.

Bartoli and Papasogli have electrolysed coke in an ammoniacal solution, but to render the liquid more conductive they added a solution of common salt. The result was the production of nascent chlorine, by which the above-mentioned products were destroyed.—*Comptes Rendus*, ciii., p. 153.

ON A PECULIAR VARIETY OF CALAMINE FROM SIBERIA.

By Dr. A. B. GRIFFITHS, F.R.S. (Edin.), F.C.S.,
and S. DREYFUS.

WE have made an investigation of a peculiar variety of zinc carbonate (calamine) which occurs in the south-west of Siberia. It is associated with barium sulphate and galena, which are imbedded in a matrix of limestone rocks.

On submitting the calamine to analysis, the crystals gave the following composition:—

Zinc	50.026	per cent.
Iron	2.773	„
Cadmium	0.921	„
Manganese	0.120	„
Silica	5.620	„
Carbonic acid	35.210	„
Water	5.330	„

100.000

This specimen of calamine had a hardness between 5 and 6, and a specific gravity of 4.629. Its crystalline form was that of a right rhombic prism belonging to the prismatic system. It was also noticed that twining amongst the crystals was not uncommon. We have never heard that calamine (ZnCO_3) has ever been found in this crystalline form before; when it is found crystallised it assumes the form of rhombohedrons. Therefore calamine appears to be a dimorphous compound, and is isodimorphous with the two crystalline forms of carbonate of calcium, namely calcite and aragonite.

Technical School, Manchester.

ESTIMATION OF CAUSTIC IN CAUSTICISED SODA LIQUOR.

By WILLIAM UPWARD.

IN the CHEMICAL NEWS (vol. liv., p. 28) appeared a short article bearing somewhat upon this subject, and written by H. Joshua Phillips. Previously to its appearance experiments on the subject had taken place in the laboratory with which I am connected for the purpose of accurately checking the workmen. As is customary at all alkali works, samples of causticised liquor are taken by us at regular intervals and tested by the BaCl_2 method. Knowing fully well that two or more chemists, experimenting upon the same samples, rarely arrive at corresponding results, the discrepancies being from two to three, or even more, per cent, we determined to try and ascertain the cause of the want of agreement. Accordingly a certain sample was selected and kept in a stoppered bottle as long as the series of tests continued. The first experiment was for the purpose of estimating the total quantity of alkali; this known, the same volume of liquor was measured, to which BaCl_2 was added, and the whole made up to 500 c.c.; half of this was then filtered and titrated. The results of seven tests was 88.68 parts of alkali as caustic per 100 of total alkali. Seven tests were afterwards made upon liquor poured off from the sediment instead of upon filtered liquor, and after treating each in a precisely similar manner we obtained 90.85 as a result. Five experiments were subsequently made upon the precipitate produced and titrating, and 91.96 was the result.

In each test distilled water that had been boiled and allowed to cool in a stoppered bottle was used. Various known quantities of BaCl_2 were also employed, and, although in some cases there was a large excess, the results were not affected.

From the facts obtained we can only conclude that it

is absolutely essential that tests be made in exactly the same way in order to secure anything approaching concordant results.

In estimating the carbonate in white caustic we weigh out about 20 grms., dissolve in H_2O , add $BaCl_2$, and place the whole in a stoppered bottle not less than one litre in capacity, and fill up to neck with hot H_2O . After complete settlement the clear liquor is syphoned off and the bottle re-filled with hot H_2O . After a second syphoning the precipitate is poured on to a filter and washed until the filtrate is freed from alkali, which does not take long after the washing in stoppered bottle. The precipitate and filter are removed from the funnel into a beaker or flask, and a known volume of standard HNO_3 or HCl in excess is run in; standard soda being employed to bring back. We find no difficulty in making two tests from one sample, with no greater discrepancy than 0.05 per cent by this method.

Deacon Road, Appleton-in-Widnes.

ON THE DETERMINATION OF ABSOLUTE NEUTRALITY.

By J. R. DUGGAN.

As some confusion exists in the use of the terms "acidity" and "alkalinity," it seems necessary to state the exact sense in which they are used in this article. It is customary to consider alkalinity as having some connection with the property of certain bodies to combine with acids to form salts and water, but this is more properly called basicity, and it is by no means necessary that a base should be alkaline, or that an alkaline body should be a base. Sodium carbonate is distinctly alkaline, but does not combine with acids, while phenol, which even has acid properties, will, under proper conditions, unite with an acid to form a salt and water. With the term acidity the difficulty is greater, because there is no other word in common use that may be used to express one of its meanings. There certainly are bodies, however, that show acid properties, but do not unite with bases to form salts, as many salts of the heavy metals; while other bodies that are neutral or slightly alkaline, will unite with bases to form salts and water, as, for example, primary alcohols. In fact, a certain substance may act as an acid or base according to circumstances, but it cannot show both acidity and alkalinity. Unless otherwise stated, the term acidity when used in this article means the opposite of alkalinity, rather than of basicity. The necessity for this distinction will, I hope, be better appreciated when the following experiments are taken into account. It must not be understood from the above that the acidity of *acids* and the alkalinity of *bases* has no connection with the *avidity to combine* or *affinity* which acids show for bases and bases for acids.*

The Influence of Mono- and Poly-basic Acids, in the Presence of their Sodium Salts, on the Conversion of Starch by Diastase.

These experiments were undertaken in order to compare the action of organic acids and alcohols on soluble ferments with their action on organised ferments, and are a continuation of some former studies on the relation between chemical constitution and physiological action.† One of the principal objects in the work was to ascertain whether or not the action of acids on diastase was proportional to their affinity. Diastase was selected because it is a typical soluble ferment, and one whose action in converting starch into dextrin and sugar is comparatively simple and easily measured. As some of the results obtained are of chemical interest, aside from any connection they may have with

physiology, it seems best to consider these separately. As the subject is still under investigation, what is contained in this article must be taken to a certain extent as a preliminary notice.

The amount of acid necessary to retard the action of diastase has been investigated by several observers, and with widely different results in each case; but the recent work of Chittenden and Cummins* has shown that this is due for the most part to the fact that different specimens of malt-extract and starch contain varying amounts of proteid matter, which combines with the acid and prevents its retarding action. They find that the acid proteids which are thus formed may even accelerate the action of the ferment. I have found that the normal salts of many acids also prevent the retarding influence of acids, just as they retard or prevent the action of acids in inverting cane-sugar.† By preparing reagents as free as possible from foreign substances, and using very dilute starch-paste, I have been able to reduce the amount of even comparatively weak acids, such as formic, that is necessary to distinctly retard diastatic action, to 0.0002 per cent (1 to 500,000) while 0.001 per cent entirely prevented action. It is evident from this that the common statement that diastase acts best in a slightly acid solution applies only to such as contains proteids or salts with which the acid may combine, and not remain free to act on the diastase. If it were possible to prepare both starch and diastase perfectly pure, it is probable that any appreciable quantity of the stronger acids would prevent the action of the ferment.

The influence of alkalies on diastase is even more marked than that of acids; so it will be seen that it is an extremely delicate indicator of acid or alkaline reaction. The practice of using litmus, phenolphthalein, and similar substances for this purpose is so common that we fall into the belief that they show absolute neutrality; but this is by no means true, and a disregard of this point must lead to grave errors in chemical and physiological investigations. A number of substances will react acid with one indicator and alkaline with another, as, for example, di-sodium phosphate;‡ or we may have an acid or base that is too weak to affect the indicator, as boric acid or urea, in which case the solution will appear neutral when it is not. We may also have a strong acid combined with such a base, or *vice versa*, so that the acid will act on the indicator as though it were uncombined, but it certainly does not act in many chemical reactions or on living organisms in such a manner. As an example, sodium borate or carbonate acts on some indicators as caustic soda, and can be titrated as such, but a more striking illustration is the titration by means of phenolphthalein of the acid combined with alkaloids as free acid.§ While sodium borate and carbonate are alkaline, they are certainly not as much so as caustic soda, and the same is true of the acid in morphine sulphate and similar salts of the alkaloids. With nearly all indicators the presence of proteid matter does not affect the accuracy with which acids may be determined, but, as already mentioned, the work of Chittenden and Cummins has shown that there is present in such cases a compound which acts entirely differently from the free acid. By the selection of indicators to suit the conditions something may be done to avoid these difficulties, but there will still remain many cases of acidity or alkalinity which cannot be measured by any of the ordinary methods. Ostwald|| has shown that each acid has a definite strength or affinity-constant which conditions the specific intensity of any action brought about by that acid. This constant may be determined by several methods, the most reliable, since it is free from secondary reactions, being based on the rate at which the acid inverts cane-sugar. It appears that each base also has its affinity-constant, although the methods by which this may be determined are not so well

* See Muir's *Principles of Chemistry*, p. 401 et seq.

† *Amer. Chem. Jour.*, vii., 62.

‡ *Studies Lab. Physiol. Chem. Yale College*, 1884-5, p. 36.

§ *Jour. f. prak. Chem.*, lxxxv., 321, and (2) xxxii., 32.

|| *Compt. Rend. de l'Acad.*, c., 55.

§ *Journ. Pharm.*, (5) xi., 425.

|| *Jour. f. prak. Chem.*, (2) xxix., 57.

developed as in the case of acids. Let us now suppose that two salts are formed by the addition of two acids to a base, as sodium chloride and sodium acetate. These salts are neutral to all colour indicators; and if this neutrality is absolute, it would seem that an equivalent of any acid can neutralise, and is neutralised by, an equivalent of any base without regard to its affinity, for these two acids differ greatly in this respect. This is the same as saying that the acid properties of an acid, and the alkaline properties of a base, are entirely destroyed when the two combine to form a normal salt. That such is not the case may be shown with the ordinary colour indicators, but only when there is very great difference in the affinities of the base and acid, as with alkaline carbonates or sulphates of some of the heavy metals. That sodium chloride does not turn blue litmus red, and sodium acetate the reverse, is due to the fact that litmus is not sufficiently delicate as an indicator to respond to the comparatively weak acid and alkaline reactions of these salts. That the salts are respectively acid and alkaline is shown beyond doubt by the investigations of Löwenthal and Lensen,* and more especially of Spohr,† on the inversion of cane-sugar, and by their influence on diastatic action in the presence of acids. The addition of sodium chloride to hydrochloric acid increases the rate at which it inverts cane-sugar, while sodium acetate has an opposite effect on acetic acid. The amount of hydrochloric acid required to retard to a certain extent (50 per cent) the action of diastase is so small that it is difficult to say if this is diminished by the addition of sodium chloride; but the increase in the amount of acetic acid that is made necessary by the addition of sodium acetate is very marked, and is proportional to the amount of the salt added. This is very well shown by the following table. The amount of conversion with diastase and starch-paste alone is shown by the control experiment. The solutions were in each case made up to 100 c.c., and the flasks containing them kept in a water-bath at 55° C. for thirty minutes, when the action of the ferment was stopped by the addition of an excess of caustic soda. The amount of sugar formed was determined volumetrically by Fehling's solution, and calculated as maltose.‡

TABLE I.

	NaOH.	C ₂ H ₄ O ₂ .	Maltose.	Per cent of retardation.
1	0.000 gram.	0.000 gram.	0.420 gram.	—
2	0.000	0.001	0.204	51.4
3	0.005	0.045	0.215	48.8
4	0.010	0.090	0.213	49.3
5	0.015	0.135	0.210	50.0
6	0.020	0.180	0.210	50.0
7	0.030	0.270	0.207	50.7
8	0.040	0.360	0.205	51.2

It will be seen that the retardation is not quite constant, but increases slightly with the amount of alkali and acid present. This is probably due to the action of the substances aside from any condition of alkalinity or acidity. This secondary action, as it may for convenience be called, is very marked with some substances, such as salts of the heavy metals, and when such is the case, of course the reaction cannot be used to measure alkalinity or acidity; but with the alkali metals and most organic substances, the error from this source is very small unless they are used in large quantities. If the retarding action of any substance is partially or entirely prevented by the presence of an acid, it seems fair to conclude that it is to that extent due to alkalinity of the substance, and *vice versa*; but when it is not affected by either acids or alkalies, it is evident that it acts on the ferment in some other manner.

The table shows that in the presence of 5 m.grms. of caustic soda, 45 m.grms. of acetic acid are necessary to

produce the amount of retardation caused by one m.grm. acting on the starch and diastase alone. (Of course the use of reagents of greater or less purity will cause the amount of acid to vary, so that more or less than 1 m.grm. may be required; and with perfectly pure materials it is impossible to say to what extent this would be reduced.) Now 7.5 m.grms., or one-sixth of the 45 m.grms. of acid, combine with the 5 m.grms. of caustic soda to form normal sodium acetate; and we must suppose that this normal salt neutralises to a certain extent the remaining 37.5 m.grms., or five equivalents of acid. In order to do this sodium acetate must be an alkaline salt, or one in which the affinity of the acid is less than that of the base. The following table shows this to be the case:—

TABLE II.

	NaOH.	C ₂ H ₄ O ₂ .		Per cent of Maltose. retardation.
1	—	—	0.428 gram.	—
2	0.020 gram.	0.015 gram. = ½ equiv.	0.000	100
3	„	0.030	1 „	0.363 15.0
4	„	0.060	2 „	0.428 0.00
5	„	0.090	3 „	0.396 7.5
6	„	0.120	4 „	0.360 15.9
7	„	0.150	5 „	0.290 32.2
8	„	0.180	6 „	0.225 47.4
9	„	0.210	7 „	0.152 64.5

The second experiment of this series is introduced to show that an excess of caustic soda acts as though there were no acetate present; that is, that the normal salt does not prevent the action of alkalies as it does that of acids. In this case one-half the soda combines with the acid, leaving 10 m.grms. free; but if such an amount of acid is used that only 1 m.grm. is left free, the result would be the same, no action taking place. In the third experiment the acid and base were added in the proportion of their combined weights, so there was present only the normal salt. This retards the reaction 15 per cent; but when another equivalent of acid is added, as in No. 4, the conversion is the same as in the control experiment, showing that the solution is neutral. When more than two equivalents of acid are added, we again get retardation from acidity.

(To be continued.)

CONTRIBUTIONS TO OUR KNOWLEDGE OF SEWAGE.

By WILLIAM RIPLEY NICHOLS and C. R. ALLEN.

IN the year 1872 one of us had occasion to report* the results of the chemical examination of a considerable number of samples of the sewage of Boston and of Worcester, Mass. The examinations then made included the determination of the nitrogen existing as ammonia or in the form of ammoniacal salts (tabulated as free ammonia), and of the nitrogen which was given off as ammonia by treatment with an alkaline solution of permanganate of potash, according to the well-known method of Wanklyn. As indicating the total amount of organic nitrogen, this last determination—that of the so-called “albumenoid ammonia”—was felt at the time to be inadequate, but under the then existing circumstances it was the best that could be done.

When Kjeldahl's process for the determination of the total nitrogen in organic substances was published a few years ago,† it suggested itself at once that the method might possibly be conveniently applied to the analysis of sewage. Circumstances have prevented, until recently,

* *Journ. f. prakt. Chem.*, lxxxv., 321, 401.

† *Ibid.*, (2)lxxxii., 32.

‡ For greater details of the method used in determining diastatic action see *American Chemical Journal*, vii., 306.

* “Fourth Annual Report of the State Board of Health of Massachusetts.” Boston, 1873. Pp. 65-81.

† *Fresenius Zeitschrift*, xxii. (1883), p. 366; *CHEMICAL NEWS*, xlvi. (1883), p. 101.

EXAMINATION OF BOSTON SEWAGE.
(Results expressed in parts in 100,000).

Number.	Date of collection.	Ammonia.	Albumenoid Ammonia.	Total Nitrogen, reckoned as		Total solids.	Chlorine.	Chlorine, reckoned as common salt.	Phosphoric Acid (P_2O_5).
				Nitrogen.	Ammonia.				
1.	1885. May 12, 7.30 p.m.	2.80	0.27	2.80	3.40	592	275	453	0.480
2.	13, 8.20 a.m.	3.18	0.44	3.46	4.20	548	258	425	0.096
3.	13, 7.20 p.m.	3.42	1.15	5.76	7.00	254	82	135	0.672
4.	14, 7.20 a.m.	1.32	0.35	1.81	2.20	570	247	407	0.704
5.*	15, 1.00 a.m.	1.29	0.87	4.63	5.62	482	133	219	1.343
6.*	15, 8.15 a.m.	1.59	0.25	6.00	7.30	416	194	320	0.512
7.	15, 4.00 p.m.	3.08	0.55	3.76	4.57	358	145	239	0.192
8.	16, 7.30 a.m.	0.95	0.55	2.14	2.60	630	311	513	0.288
9.	17, 4.25 p.m.	5.68	5.96	14.53	17.65	554	215	354	7.035
10.	18, 8.00 a.m.	6.23	5.84	13.82	16.78	528	?	?	6.490
11.	24, 7.50 p.m.	11.94	3.32	17.15	20.82	178	59	97	3.325
12.	23, 12.40 a.m.	?	2.62	4.32	5.30	378	178	293	0.992
13.	26, 12 hr. day average†	5.71	4.22	11.32	13.75	460	177	292	4.893
14.	27, 12 ,, ,, ,, †	5.71	3.31	9.55	11.60	640	288	475	6.188
15.	28—29, 24 ,, average‡	3.13	5.49	9.82	11.93	588	240	396	4.702
	1872. Average of 33 day samples§	2.72	0.73	—	—	59	19	31	1.69
	,, ,, 4 night ,,	1.33	0.23	—	—	17	4.5	7.4	—

* Samples 5 and 6 contained a good deal of storm water. † Samples taken every four hours. ‡ Samples taken every two hours.

§ Samples from sewers near the water front, which evidently contained much sea-water, were not included in these averages.

|| Average of 19 samples.

the carrying out of this idea; meanwhile the process has found extensive application, especially in agricultural laboratories, and has been used in the analysis of certain kinds of fertilisers. It is possible that it may have elsewhere been applied to the examination of sewage; if so, we have failed to meet with notice of such application, which we find to be quite practicable and to give satisfactory results.

In order to familiarise ourselves with the process and, at the same time, to become satisfied of its substantial accuracy, determinations of the total nitrogen were made in sulph-urea, in dried and powdered horse-dung, and in dried and powdered human excrement, the amount of nitrogen being checked either by theory or by an absolute determination, according to Dumas's method. The results were as follows:—

	I.	II.	III.
	Kjeldahl's Method.	Dumas's Method.	Theory.
Sulph-urea	36.89 per cent	—	36.84
Horse-dung. 1 ..	3.16 „	3.28	—
„ 2 ..	3.12 „	—	—
Excrement	6.20 „	6.08	—

In order to satisfy ourselves as to the constancy of the results obtained in a number of determinations made on the same sample of actual sewage, a sample was procured and analysed with the following results.

Organic Nitrogen expressed as Parts in 100,000.

Kjeldahl (after deducting nitrogen as free ammonia).	Dumas.
3.75	3.66
3.50	—
3.75	—
3.70	—
3.75	—
3.75	—
3.80	—

It thus appears that the process gives uniform results, and that these results are sufficiently accurate for the purpose. It has the advantage of requiring only the ordinary apparatus used in water analysis, as generally conducted in this country, and of avoiding a dry combustion, which, in the simplest form, is more or less troublesome, especially where a liquid has to be evaporated,

and the solid residue transferred from the evaporating dish.

There is little doubt that the coming decade will see in this country a considerable application of the method of disposing of sewage by irrigation, and it seems to us that Kjeldahl's process will afford a ready means of determining the amount of that important constituent—the combined nitrogen. The process, as we have used it with sewage, is as follows:—

From 25 to 50 cubic c.c. of sewage are introduced into a small flask, preferably flat bottomed, made acid with sulphuric acid, and evaporated to dryness on a water-bath. This is best and most rapidly accomplished by drawing through the flask a somewhat rapid current of air which has been freed from moisture and ammonia by bubbling through strong sulphuric acid. We have satisfied ourselves that the loss of “free ammonia” by this treatment is inappreciable, so that the residue contains the total combined nitrogen* of the sewage. This residue is treated in the flask with 5 c.c. of fuming sulphuric acid, which is run in from a glass-stoppered burette. The flask is placed on a piece of wire-gauze over a small gas-flame and heated until a light yellowish brown liquid is obtained. With sewage this result is sometimes reached in half-an-hour; usually from one to two hours are required. Permanganate of potash is then added to complete the oxidation, a few crystals being sufficient.†

The contents of the flask are then washed into the distilling apparatus with about 500 c.c. of pure distilled water, enough caustic potash is added to give an alkaline reaction, and the nitrogen, which is now all in the form of ammonia, is distilled off in the usual way. The distillate is made up to 250 c.c. and aliquot portions are nesslerised as in water analysis. As the sulphuric acid usually contains a trace of nitrogenous compounds, a blank experiment determines a slight correction to be applied.

The process as just given may be modified by evaporating the sewage without first acidulating with sulphuric acid. The evaporated water may be condensed and the free ammonia determined therein and an approximate determination of the total solids may be made by using a tared flask. We prefer, however, to proceed as indicated above and to make a separate determination of free ammonia, with which may be coupled, if desired, a determination of the so-called albumenoid ammonia.

* The nitrogen which exists in the sewage as nitrites and nitrates is too small to be of practical importance, although there is usually a trace.

† For fuller details, see Kjeldahl's original paper, referred to above.

Boston Sewage.

Since the examinations of sewage made in 1872, the Boston system of sewerage has undergone an entire change. Instead of being discharged from short sewers emptying at intervals along the water-front, the sewage is now collected into one encircling sewer, carried by means of a tunnel to Moon Island, and allowed to flow into the outer harbour on an ebb tide.

We have examined a number of samples taken from the pumping station at City Point, where the sewage is lifted in order that it may flow through the tunnel to Moon Island. The sewage was received as a rule in a fresh condition; the heavier suspended particles were allowed to subside, and no attempt was made to determine their amount. In fact, the determination of suspended matters in small samples is of little value, and a more practical idea of their amount could be obtained on a large scale by estimating the amount deposited in the settling-tanks. The following table contains the results of the examination of various samples of sewage from the pumping-station. It will be noticed that the samples taken at different times vary very much from each other. The large amount of total solids and chlorine are said to be due to the fact that a considerable quantity of sea-water is used in certain manufactories for cooling purposes and to the infiltration of salt water into the sewers which are below the tide level.

Nitrogen as Urea.

The rapidity with which urea is converted into carbonate of ammonia and water in the presence of the urea ferment which is probably always present in sewage, would prevent its existence in stale sewage, but as the Boston sewage reaches the point from which our samples were taken in a fresh condition, we might expect to discover some of this substance still unchanged.

The evidence that urea was present in several samples which were tested is as follows:—Two portions of 50 c.c. each were boiled in small flasks to expel the free ammonia and to kill any of the ferment present, and the necks of the flasks then stopped with cotton-wool. When the contents had become cool one of the flasks was infected by dipping a glass rod first into a fermenting solution of urea, or into stale sewage, and then into the boiled sample. The two samples were allowed to stand side by side for several days, and then examined for free ammonia in a similar fashion. In one case the flask which had not been impregnated was free from ammonia; generally, however, a small amount of ammonia had developed itself; in all cases the impregnated flasks showed a much greater amount of ammonia than was contained in the companion flasks. This certainly points to the presence of urea or some similar fermentable nitrogenous compound in the sewage as it reaches City Point.

In conclusion we desire to acknowledge our indebtedness to the Department of Improved Sewage for facilities in collecting samples, especially to Mr. Barnes, at Chester Park, and to Mr. M. H. Holmes, at the pumping-station. —*Journal of the Franklin Institute.*

NOTICES OF BOOKS.

The Gas Engineer's Chemical Manual. By J. A. WANKLYN. London: The Scientific Publishing Company, Limited.

THE author remarks truly enough in his preface that we must "look to a wide development of the gas industry for the abatement of the smoke nuisance, and for the bringing back of vegetation into many of our towns." But before so desirable a consummation can be reached coal-gas must be purified from sulphur compounds to a far greater extent than it has hitherto been found practicable. It is a familiar observation that plants do not thrive in

rooms lighted with gas. It is possible, however, that if the "coal-liming process" noticed in the last chapter of this manual is fairly carried out we may have the convenience of burning a gas free from sulphur.

In the section on coal attention is called to a determination of the percentage of unoxidised hydrogen as found by taking one-eighth of the percentage of oxygen and subtracting it from the percentage of hydrogen. In this important respect Lancashire coal does not maintain its traditional reputation as a gas coal. It is surpassed not merely by certain Scotch cannel, but by the Haswell Wallsend, and by one sample from Wales and one from Somersetshire.

In the chapter on coal-gas Mr. Wanklyn advises the determination of sulphuretted hydrogen, ammonia, the oxides of carbon, the special illuminants, such as benzene, carbon disulphide, and organic sulphur compounds. For estimating the illuminants he recommends that the gas should be submitted to the solvent action of a limited quantity of rectified spirit, the decrease of volume being noted after the alcohol has been eliminated.

In speaking of carbon dioxide the author mentions the excessive proportion of this formidable poison in so-called "water gas," i.e., the gas produced by the action of steam upon red-hot coke, as a serious objection to the use of such gas. A fatal objection it doubtless is unless escapes could be absolutely excluded.

Mr. Wanklyn mentions the absolute suppression of carbon monoxide in coal-gas as a desideratum. So it is, but we fear that the successful inventor will find his patent expired before the process is adopted.

The scheme for what may be called the practical testing of coal-gas, as distinct from the complete analysis, is claimed as being, "in a subordinate sense," new and original. It appears likely to meet the demands of the managers of gas works. Particular attention must be called to the method proposed for the volumetric determination of hydrogen sulphide in crude gas, a standard solution of lead acetate being employed.

Among the good features of this work must be mentioned the total absence of "padding." Practical men will not have to seek for the author's meaning amidst a wilderness of unnecessary verbiage. We may safely recommend it as a useful addition to the literature of a subject which is increasing in importance.

CORRESPONDENCE.

RADICAL OR RADICLE?

To the Editor of the Chemical News.

SIR,—I quite appreciate the points urged by Prof. Divers (CHEM. NEWS, vol. liv., p. 36) in favour of the first of the above modes of spelling the word, but I cannot admit that they apply to this particular case.

The words ending in *-al*—of which he gives a list—are, with the exception of *menial* (which has an interesting history of its own), and *chemical* (which would hardly be used as a substantive in any decently-written scientific paper), English adaptations of well-recognised Latin words, e.g., "*principalis*." But there is no substantively-used adjective "*radicalis*" in the whole range of Latin literature, so far as I am aware: not even in the late monkish stuff which finds a place in Ducange's *Glossarium*.

If there was anything to be gained in euphony or conciseness by making the word end in *-al* instead of *-cle* (compare the celebrated controversy about "telegram" and "telegraphene"), it would be a different matter. But since this is not the case, we may just as well spell the word in the etymologically-correct way, as copy an erroneous Gallicism.—I am, &c.,

H. G. MADAN.

Eton College, July 30, 1886.

PATHOGENIC MICRO-ORGANISMS IN WATER.

To the Editor of the Chemical News.

SIR,—Referring to the Report on the London Water Supply published in your last issue, I would venture to offer a few remarks on the mention which is here made of experiments on the vitality of the *bacillus anthracis* in water. From the Report it does not appear whether the experiments have been made with the *bacilli* or the *spores* of anthrax, which, as is well-known to students of bacteriology, are endowed with such very different powers of resistance to hostile conditions. From the results obtained, however, it would appear that the *bacilli* only, and not the *spores*, had been the subject of experiment, for Dr. Meade Bolton, who has recently published a paper in which he deals with the behaviour of anthrax in both its forms in various kinds of water, has shown that, although the *bacilli* rapidly become extinct in some kinds of potable water, the *spores*, on the other hand, retain their vitality even in distilled water for upwards of ninety days, whilst in polluted well-water they were unimpaired after nearly a year. The vitality of pathogenic microbes in water is a subject of great interest, and I have myself been much struck with the differences in behaviour in this respect which are exhibited by specific pathogenic micro-organisms. The results of my experiments with Koch's "comma" spirillum, Finkler-Prior's "comma" spirillum, and the *bacillus pyocyaneus*, were communicated to the Royal Society in June last. I have found that whilst the *bacillus pyocyaneus* flourished under almost every condition to which it was exposed, the two others were far more sensitive—the Finkler-Prior spirillum, in fact, being so in such a high degree that in no case was I able to demonstrate its presence in water after the first day of its introduction, whilst Koch's "comma" spirillum could not be demonstrated in the purest forms of potable water after the ninth day, but in sewage it underwent enormous multiplication for upwards of twenty-nine days.—I am, &c.,

FERCY F. FRANKLAND.

Normal School of Science,
South Kensington Museum, S.W.,
July 28, 1886.

SCIENTIFIC EXPERTS IN PATENT CASES.

To the Editor of the Chemical News.

SIR,—Perusing your remarks in reference to the employment of scientific experts in cases of patent infringements, with your permission I will offer a few remarks. The practice has grown, and it must be admitted as inevitable, that such disputes when they occur will have to be settled by scientific opinion; but our present mode of procedure is an expensive one. Highly paid scientific experts are employed to coach counsel also highly paid, on both sides, and naturally on which ever side these may be engaged, their inclinations, in spite of themselves, would sway to that side; with an equal array of talent opposed, some may say it is as fair for one as another, but is it always so? An inventor may have to fight powerful moneyed interests, or trade combinations, and, short of the wherewithal, he runs the risk of suffering grave injustice. These Patent cases are becoming a public calamity, and are knocking the heart out of many earnest inventors; and as the benefits accruing to the world are in a very large measure the result of invention, in some shape the crippled condition, or possibly the ruin, of an inventor brought about by the effort to prove his rights, is a discouraging matter to more than one inventor. These disputes are the result of monopolies. Rightly or wrongly, the public look on a patentee as a monopolist, but he is of no account until his invention is proved of utility and a demand springs up for it; when the greedy and watchful competitor feels it intolerable he should be shut out of it and distanced completely. Failing to bring something out better, he produces a bad imitation or a questionable im-

provement, and war commences, ending in a case for the law courts. There the lawyers and experts nurse the matter, and turn it out of hand with quite a new complexion, such as neither of the contending parties themselves ever experienced (and presumably they should know most about it). If to foster inventive talent is to improve our trade, it is surely the interest of all inventors to combine with the friends of invention and try to secure a better protection of their interests. The State has no business in allowing the title of "true and first inventor" under the present inadequate and non-technical mode of examining Patents. It is utterly wrong in accepting fees and granting so-called "protection" and refusing to stand by its own acts. It is equally at sea in granting patents, and an unrestricted right to patentees to charge whatever they like to the public for their inventions, encouraging in many cases these irritating monopolies. Its gravest fault is, perhaps, that it fails to recognise it is a public duty to ascertain the novelty of inventions, and if these are reasonably proved on technical examination, to grant a patent at the lowest compatible cost, and *having granted it*, after giving the public a voice in the matter, the State should support its act.

The fear of complication is dispelled by provisions for the public also to make use of the inventions on fixed terms (not fixed by the patentee alone). Hence it is obvious, where all have the same privileges, a monopoly cannot exist; for the Royalties which are fixed by a reasonable scale are only to be considered as the just reward and encouragement given to the inventor for producing his invention. Piracy might try to profit still, but it would receive its deathblow in that it would be the interest of all concerned in the invention (independently of the inventor himself) to expose it, and the State could punish and claim arrears, as they would an evasion of income-tax. The suggestions put forth have been discussed, and with me maintain their reasonableness. I should be glad of any better method to attain the object in view, and reduce the number of expensive patent cases. Apologising for trespassing on your space,—I am, &c.,

CHAS. HOWIE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 3, July 19, 1886.

Displacement of Ammonia by Other Bases and its Determination.—MM. Berthelot and André.—The author's experiments prove the difficulty and tediousness of displacing ammonia in its double salts. They prove that magnesia, and in certain cases even lime, is incapable of entirely displacing ammonia in the cold or even on boiling for some hours. Salts which have undergone the action of magnesia, if further treated with dilute boiling soda, retain a notable proportion of their ammonia, which can be entirely eliminated only by the action of soda-lime at a red-heat. Calcium hydroxide itself at 100° and on prolonged boiling only expels a part of the ammonia in ammonium-magnesium phosphate. In the cold the action of lime is prolonged indefinitely in presence of this salt. Soda alone is quite effective at 100° in presence of magnesium salts, though much more slowly than with ammonium chloride. In the cold its action is almost interminable. Soda mixed previously with magnesia acts with the above-mentioned salts almost like pure soda. But if magnesia is first used alone soda remains unable to complete its action. These circumstances must be

taken into account in the analysis of soils, &c., containing organic matters along with phosphates or magnesia.

Variations of the Absorption Spectra in Non-isotropic Media.—H. Becquerel.—Not susceptible of useful abstraction.

Decomposition of Hydrofluoric Acid by an Electric Current.—H. Moissan.—Already inserted.

Urethane from an Analytical Point of View.—G. Jacquemin.—Experiment proves that 0.10 gm. of urethane dissolved in 10 c.c. of mercury and mixed with an excess of potassa is entirely precipitated by a 10 c.c. of a standard solution containing 30.44 gm. mercuric chloride per litre. The end of the process is marked by the distinct appearance of a persistent yellow precipitate of mercuric oxide, preceded by a very faint yellowish tint, which, with a little practice, is easily distinguished. Mercuric nitrate and acetate behave with urethane in presence of potassa like the chloride. These two salts, which precipitate urea at once but throw down urethane only with the assistance of potassa, are, therefore, differential reagents for these two compounds. This method is applicable to the detection of urethane in urine. Normal urine, even when much diluted with water, gives by this reaction a white precipitate which blackens on ebullition. The urethane is, therefore, extracted from the specimen of urine by shaking with ether, giving it at least 300 shakes. After decantation it is repeatedly washed with water. The residue, after evaporating the ether, is taken up in a little water and treated as above. By making use of the standard solution of mercuric chloride the weight of urethane extracted from a given volume of urine may be ascertained. Albumen and the yolk of egg, if separated and heated with urethane at 30°, decompose it in a manner analogous to aqueous potassa, but the liberation of ammonia is infinitely less. After a prolonged action there is found neither urea nor urethane.

Action of Certain Organic Chlorides upon Diphenyl in Presence of Aluminium Chloride.—P. Adam. The action of methylene chloride has yielded fluorene. Methyl chloride yields, under similar circumstances, a great number of derivatives, the study of which the author has not yet completed.

On Normal Propylamines.—C. Vincent.—The author has separated the three normal propylenes as obtained by Hofmann's general process. He has described nitrosodipropylamine and dipropylamine, and determined the physical constants of di- and tri-propylamine and of nitrosodipropylamine.

A New Creatinine, Ethyl-amido-aceto-cyamidine, and the Formation of Creatinines and Creatines.—E. Du villier.—From the results of these experiments it appears probable that the action of cyanamide upon the amidated acids consists essentially in the formation of creatinines, the formation of creatines occurring only in a small number of cases. It is even probable that the amidated acids derived from the ammonias higher than ethylamine, or from more complex bases, will yield merely creatinines.

Combination of Stannic Chloride with Hydrochloric Acid.—R. Engel.—The compound obtained by the author is a chlorostannic acid answering in its composition to chloroplatinic acid.

On Potassium Alcoholate.—E. J. Maumené.—The crystalline alcoholate, prepared in an atmosphere of hydrogen, is perfectly colourless, and yields 47 grms. of potassa, fused at redness, to 116 of alcohol.

Zeitschrift für Analytische Chemie.
Vol. xxv., Part 3, 1886.

Modification of Sonnenschein's Method for Determining Phosphorus in Iron and Steel.—N. Huss.—This paper will, if practicable, be inserted in full.

On Azotometry and Azotometers.—W. Knop.—An illustrated paper.

Analysis of the Hot Springs of Leuk.—G. Lunge and R. E. Schmidt.—This memoir, which requires the three accompanying illustrations, deals with a subject of little general interest.

Determination of Nitrogen in Coal and Coke.—Sigismund Schmitz.—The method of Dumas, which is very tedious and requires great dexterity, has the disadvantage that coal and coke are burnt imperfectly in an atmosphere of carbonic acid, even at a full white heat. The tension in the glass tube is often so great that it blows out or bursts. The Varrentrap-Will method gives results which are too low in case of coal and quite false in case of coke. The author recommends Kjeldahl's process as modified by Stutzer and Reitman.

Criticism of the Direct Methods for Determining Tartaric Acid in Argols and Lees of Wine.—Dr. A. Bornträger.—A treatise of nearly 40 pages, and not capable of useful abridgment.

Determination of Ferric Oxide in Presence of Alumina.—E. Donath and R. Jeller.—In such determinations the iron is generally determined volumetrically by Marguerite's method and the alumina calculated as difference. This procedure, however, is somewhat tedious, whence the author suggests the following modification:—If ferric oxide is ignited in a covered porcelain crucible along with zinc-powder or very fine zinc filings, there ensues an energetic reaction. The ferric oxide is completely reduced to metallic iron and the black-grey spongy mass, which is found under the white crust of zinc oxide, dissolves in dilute sulphuric acid (1 part to 2 or 3 water), even in the cold, but more readily on heating. In this manner a ferrous solution is quickly obtained, containing all the iron in the ferrous state, and it may be at once, after suitable dilution, titrated with permanganate. In practice the mixture of ferric oxide and alumina, as obtained in the course of an analysis, is ground up in a porcelain crucible with from $\frac{1}{2}$ to 1 volume of zinc powder, covered with a small quantity of fine zinc filings, closed with the lid, and strongly ignited for five to eight minutes. The mass, when cold, is easily removed from the crucible and is placed in a flask. The residues adhering to the crucible and the lid are dissolved off with the dilute sulphuric acid as above mentioned, rinsed into the flask, and the contents of the latter are heated to a boil after a further addition of dilute sulphuric acid, which is effected in from ten to fifteen minutes. As regards the zinc, zinc powder is preferable on account of its more energetic action. It contains, however, traces of iron and other substances capable of reducing permanganate, the quantity of which must be previously determined and deducted. Filings obtained from pure zinc can be freed from a mechanical admixture of iron by means of a powerful magnet. "Zincum pulveratum purissimum" has been found useless from containing several per cents of tin. As alumina and chromium oxide are not reduced by ignition with zinc the behaviour of ferric oxide may also be used for the gravimetric separation of these bodies, analogous to Rivot's method. The author remarks in a note that the attempts to render chrome iron more easily soluble in acids by ignition with zinc powder gave negative results.

Improvements in Combustion Furnaces.—Julius Schober.—This paper requires the three accompanying cuts.

Apparatus for Washing and Drying Precipitates with the Most Complete Exclusion of Carbonic Acid and Air.—Ad. Jolles.

Apparatus for the Volumetric Determination of Nitrogen.—Ad. Sonnenschein.

Desiccation of Fats.—Ad. Sonnenschein.—These three papers cannot dispense with the accompanying illustrations.

Normal Volumetric Solutions and the Retention of Mohr's System.—B. Tollens.—The writer protests against Winckler's proposal to double the strength of normal solutions as calculated to produce confusion.

Kipp-Wartha's Sulphuretted Hydrogen Apparatus.—J. Meister.—The author points out that the glass cock connecting this, the upper vessel, with the space where the gas is liberated easily gets out of order, and he proposes certain improvements.

Application of Metallic Hydrogen in Analytical Chemistry.—Schwarzenbach and L. Kritschewsky.—By metallic hydrogen the authors understand such as has been absorbed by palladium. Proceeding from the observation of Graham that such hydrogen possesses a remarkable reductive power, they have examined in how far it may be used for analytical purposes. They found by preliminary experiments that by this means silver, mercury, gold, platinum, palladium, and copper can be thrown down in the metallic state. Manganese in the form of permanganic acid is reduced in presence of free acid to a manganous salt, ferric to ferrous salts, chromic acid to chromium oxide. Potassium chlorate is transformed into the corresponding hypochlorite, acetic acid into alcohol and aldehyd, nitrobenzol into aniline. The salts of lead, bismuth, cadmium, arsenic, antimony, tungsten, molybdenum, zinc, cobalt, nickel, aluminium, cerium, uranium, rubidium, caesium, as well as of the other alkalis and alkaline earths, are not reduced. The authors used a thin rolled plate of palladium or a wire weighing 3 to 4 grms., saturated with hydrogen by the galvanic process. It is carefully washed and dried and is placed in a very dilute aqueous solution of the salt to be decomposed.

On Fractionated Distillation.—Improved processes have been proposed by E. Claudon (*Soc. Chimique de Paris*), D. Mendeleeff (*Ber. Deutsch. Chem. Gesellsch.*), F. Rasinski (*Journal für Prakt. Chemie*), and Lazarus (*Ber. Deutsch. Chem. Gesellsch.*).

Opening up Silicates by Means of Alkaline Carbonates.—Fr. Stolba.—The silicate is mixed in the usual manner with four parts of sodium carbonate and ignited until it undergoes no further change. The ignited mass is then covered with $\frac{1}{2}$ to 1 vol. of sodium chloride, which has previously been allowed to decrepitate, and heated in the covered platinum crucible until it flows quietly. As soon as the contents of the crucible have become a thin liquid they are poured out upon any suitable slab, and when cold enough they are boiled in water. The mass quickly dissolves and is then subjected to further treatment as usual.

Spectroscopes.—H. Kruss and K. W. Zenger have proposed improvements in these instruments. Zenger dispenses with the slit and the collimator lens and uses in their stead a vertical cylindrical mirror.

Polarising Apparatus.—Th. and A. Dubosq and also C. Reichert have proposed modifications in this apparatus, and which are here figured.

A Lamp for the Production of the Sodium Flame.—H. Landolt.—For a description of the proposed arrangement the reader is referred to the original.

A Rotatory Microscope Stage Capable of being Simultaneously Heated.—R. Schulze.—This apparatus cannot be intelligibly described without the illustration.

Thermo-regulators, Thermostates, and Pressure-regulators.—A series of appliances are here described and figured.

Apparatus for Extracting Liquids with Volatile Solvents.—G. Neumann.

Apparatus for Extracting Solids.—Th. Weyl.—Both these papers require the accompanying illustrations.

Modification of Glaser's Combustion-Furnace.—R. Anschütz and A. Glaser.—The lower part of the side-walls is composed not of clay, but of mica. The set of

burners in the new furnace slides in a groove and can be drawn out if needful. This arrangement not merely facilitates repairs but renders it possible to expose every part of the combustion tube to the full action of the flames. This modification is especially adapted for Kopfer's method of elementary analysis.

Modification of the Will-Varrentrap Bulb Apparatus.—C. Arnold.—The construction of this apparatus is shown in the accompanying figure.

Aerostatic Balance for Determining the Specific Gravity of Gases.—E. Lommel.—This instrument depends on the same principle as the ordinary hydrostatic balances and consists of a balance to one end of which a hollow glass globe of known weight is suspended by a fine wire. The latter passes through a fine aperture in the lid of a glass cylinder within which is the glass globe. The cylinder can be filled with different gases through lateral apertures.

Vacuum-Exsiccator with Arrangements for Heating.—R. Anschütz.—From *Liebig's Annalen*.

Pressure-Bottle for Determining Starch.—H. Rempel.—The large frame-work of Lintner's original bottle is suppressed and the arrangement for securing the pressure-plate is fixed only to the neck. Instead of the paraffin-bath he uses an air-bath.

A Gas Generator.—R. Schulze.—This apparatus, which cannot be intelligibly described without the accompanying figure, is calculated to produce a constant stream of gas from powdery materials.

Filter of Asbestos Paper.—A. Convert.—The author recommends this paper for many purposes. In many cases it is well to shake up the turbid liquid with fragments of asbestos-paper and then to pour it through an asbestos filter.

Arsenical Chloride of Lime and Potassium Chlorate.—L. Garnier.—Noticed under *Journal de Pharmacie et de Chimie*.

Production of Hydrogen Sulphide free from Arsenic.—Otto v. d. Pfordten.—The author generates the gas by the action of hydrochloric acid upon ordinary iron sulphide, passes it over a desiccating agent, and then into a tube 30 centimetres in length filled with unbroken pieces of potassium sulphide and placed in an air-bath at 350°, and finally through a washing-bottle containing solution of soda. F. Gerhard utilises the process of obtaining hydrogen sulphide by heating magnesium hydrosulphite, first proposed by Divers and Shimidzu. He obtains the magnesium hydrosulphide by the double decomposition of alkaline sulphides or hydrosulphides, or calcium sulphide with magnesium salts. The entire mixture is gently heated, and yields an equable current of gas easily regulated. H. Hager, in order to obtain hydrogen sulphide free from arsenic, uses pure zinc sulphide and hydrochloric acid. The zinc sulphide is obtained by boiling corresponding quantities of zinc oxide or zinc sulphate and sulphur with an excess of soda-lye. The liquid is poured off, the damp mass is mixed with 1-10th of its bulk of white bole and moulded into small rods which are preserved for use. A gentle heat must be applied if a rapid current of sulphuretted hydrogen is required.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Sulphide of Molybdenum.—Will anyone oblige me with the title of a most comprehensive work published on sulphide of molybdenum and its compounds.—J. A. M.

THE CHEMICAL NEWS.

VOL. LIV. No. 1394.

ON SILVER CARBONATE.

BY GEORGE STILLINGFLEET JOHNSON.

THIS compound, as obtained by precipitation of solution of silver nitrate by an alkaline carbonate, is white at first, but becomes yellow when the soluble salts are washed out (Berzelius). According to H. Rose (*Ann. Chem. Pharm.*, lxxxiv., 202), silver carbonate loses carbonic anhydride at 200° C., leaving pure oxide of silver, which begins to evolve oxygen when the temperature is further raised to 250° C.

In "Phillips's Mineralogy," 1852, the mineral *Selbite* is mentioned as a native carbonate of silver, having the composition—

" Carbonic acid	12.0
Silver	72.5
Carbonates of oxides of Sb with Cu..	15.5
	100.0

Found at St. Wengel's mine in the Black Forest, and in Mexico. Dana also mentions it as a rare mineral. It is described as amorphous, earthy, opaque, and grey.

If the above represents—as I believe it does—the present state of our knowledge regarding this compound, the following observations which I have recently made respecting it cannot be wanting in interest or importance.

Having occasion for some pure silver oxide, I poured a hot solution of silver nitrate into a hot concentrated solution of potassic hydrate (prepared by alcohol), and washed the heavy brown precipitate by decantation many times with boiling water.

The greater part of the pure silver oxide thus prepared was consumed to remove chlorine from an organic solution, but a portion of it was left in the beaker in which it had been precipitated, covered with distilled water, whilst the mouth of the beaker was closed only by a loosely-fitting dial-glass to exclude dust.

After about two months, during which time the beaker and its contents had remained undisturbed, the water with the precipitate was poured off into another vessel, when the bottom of the beaker was found covered with large glistening yellow crystals,* which were detached carefully and separated as completely as possible from the unaltered silver oxide.

On treating a portion of the crystalline matter with diluted nitric acid, it dissolved immediately with abundant effervescence, whilst the solution gave a curdy white precipitate with hydrochloric acid. When laid upon moistened reddened litmus-paper, the crystals showed an alkaline reaction, which disappeared on drying. When heated in a glass tube, the crystals first became purplish-black, then fused at a little below a red heat, and immediately afterwards evolved abundance of gas, leaving a white mass of pure metallic silver, which when soaked with water did not impart the slightest alkaline reaction to that liquid, so that the yellow crystals are thus proved to have been quite free from any carbonate of an alkali metal. 0.090 grm. of the crystals left 0.070 grm. of metallic silver, corresponding with 77.78 per cent of Ag. The formula Ag_2CO_3 requires 78.26 per cent of Ag. The yellow crystals appear, therefore, to be silver carbonate. Examined under an inch object-glass, their form seemed to be prismatic with a tendency to tabular arrangement (thin plates). Next to the crystalline form of this compound,

its most striking property is its *fusibility*, and I was the more surprised at this, as neither Berzelius nor H. Rose (*loc. cit.*) makes any mention of it; and, indeed, the statement of Rose that silver carbonate decomposes at 200° C., leaving pure silver oxide, is quite contrary to my own observations. To settle this point—the action of heat upon silver carbonate—I next prepared some of the compound by precipitation of silver nitrate with sodium carbonate and thorough washing by decantation.

Examined under the microscope, the precipitate was quite amorphous. As regards colour, the statements of Berzelius are quite correct. It is first white, and becomes yellow on washing.

Heated in a glass tube, the precipitated carbonate behaved exactly like the crystalline compound; it fused at a little below a red heat, having given off no gas previously, but only undergoing a darkening of colour, and immediately after fusion it tumultuously decomposed, leaving metallic silver. Some of the dry precipitated silver carbonate was heated in a glass tube in a oil-bath with a mercurial thermometer immersed in the oil. The temperature was raised to 350° C., but though carefully watched the whole time, no change was observed, except a darkening of colour, and when subsequently heated over a flame as before, the carbonate fused and behaved as usual. I would, therefore, modify the statement of H. Rose regarding the action of heat upon silver carbonate—thus, it fuses at a low red heat, and is shortly afterwards decomposed tumultuously.

In order, if possible, to throw light upon the mode of formation of the crystalline silver carbonate, the following experiments were conducted.

Some of the pure well-washed precipitated silver carbonate, prepared as above, was suspended in distilled water at the temperature of the laboratory, through which a slow stream of carbon dioxide gas was kept passing for about six hours, the suspended carbonate being frequently stirred up during the passage of the gas. On separating the undissolved carbonate I obtained a colourless brilliant filtrate, which hardly produced any change in the colour of blue litmus-paper. On boiling a portion of this solution a yellowish precipitate of silver carbonate was thrown down. Hydrochloric acid, of course, precipitated silver chloride. 500 c.c. of the filtered solution of silver bicarbonate, prepared as above, was precipitated by HCl, and the weight of silver chloride formed was estimated as usual.

0.440 grm. of AgCl was obtained, which corresponds with 0.423 grm. of Ag_2CO_3 .

From this it follows that a litre of water saturated with carbon dioxide gas at about 15° C. will dissolve 0.846 grm. of pure precipitated silver carbonate.

It is interesting here to remark that, according to Lassaigne (*J. Chim. Méd.*, 1848, p. 312), water saturated with carbon dioxide at 10° C. dissolves $\frac{1}{1136}$ th of its weight of *calcium carbonate*, which is equivalent to 0.8802 grm. CaCO_3 per litre, so that, by a curious coincidence, the actual weights of silver and calcium carbonates, dissolved by water saturated with carbon dioxide gas, are nearly identical.

A portion of the solution of silver bicarbonate was left exposed to the air at the ordinary temperature for 12 hours, after which a little yellowish precipitate was found in suspension. Examined under a $\frac{1}{4}$ inch object-glass, this precipitate was seen to be crystalline and quite homogeneous, the crystals having exactly the form and appearance observed in the case of the larger ones produced by the gradual carbonation of silver oxide suspended in water exposed to common air.

It is possible that the solution of silver bicarbonate might be useful in medicine as a mild preparation of silver, less likely to produce local irritation when exhibited internally than the nitrate.

In the fusibility and alkalinity of its *carbonate*, silver resembles the alkali-metals; whilst the greater solubility of its *bicarbonate* reminds us of the alkaline earths.

King's College, London, August 2, 1886.

* Roscoe and Schorlemmer, in their "Treatise on Chemistry" (vol. ii., Metals, Part I, p. 379), mention that "when a mixture of ammonio-nitrate of silver and potassium hydrate is exposed to the air, silver oxide separates out, and after a time lemon-yellow needles of the carbonate."

ON RADIANT MATTER SPECTROSCOPY.*

PART II.—SAMARIUM.

By WILLIAM CROOKES, F.R.S.

(Concluded from p. 66).

The Delicacy of the Spectrum Test for Samarium.

156. THE foregoing observations had prepared me for the exceeding delicacy of this spectroscopic test for samarium. Experiments were now commenced with the object

samarium to 100 parts of calcium. The spectrum (Fig. 15) was very brilliant, and but little inferior in sharpness to the spectrum given by a 50 per cent mixture.

158. A mixture was now prepared containing 1 part of samarium to 1000 parts of calcium. Very little difference could be detected between the spectrum of this mixture and that of the last. The bands were, however, a little less sharp. Fig. 16 shows the appearance of this spectrum.

159. A mixture containing 1 part of samarium to 10,000 parts of calcium. The resulting spectrum is shown in

FIG. 15.

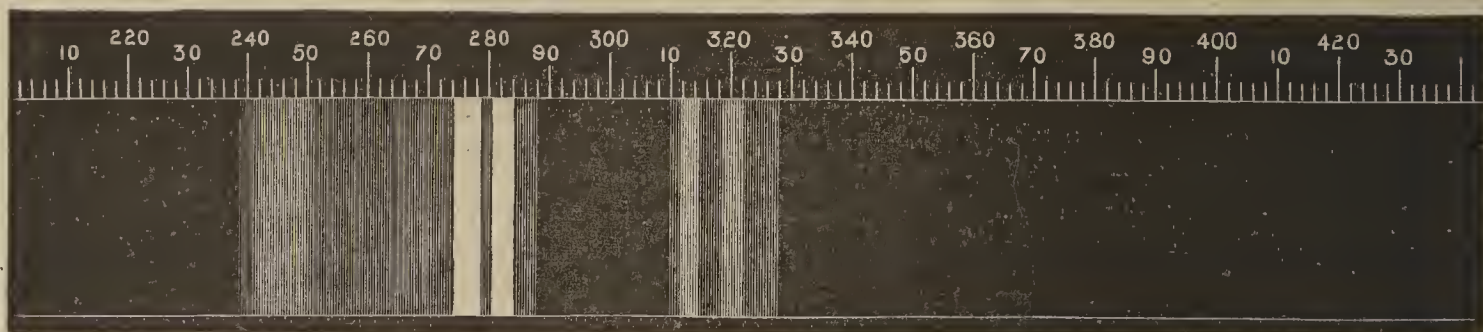


FIG. 16.

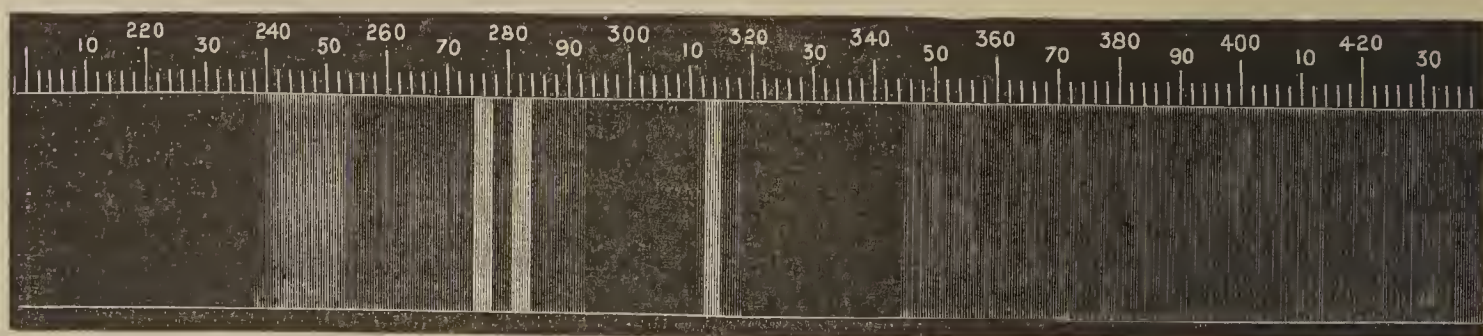


FIG. 17.

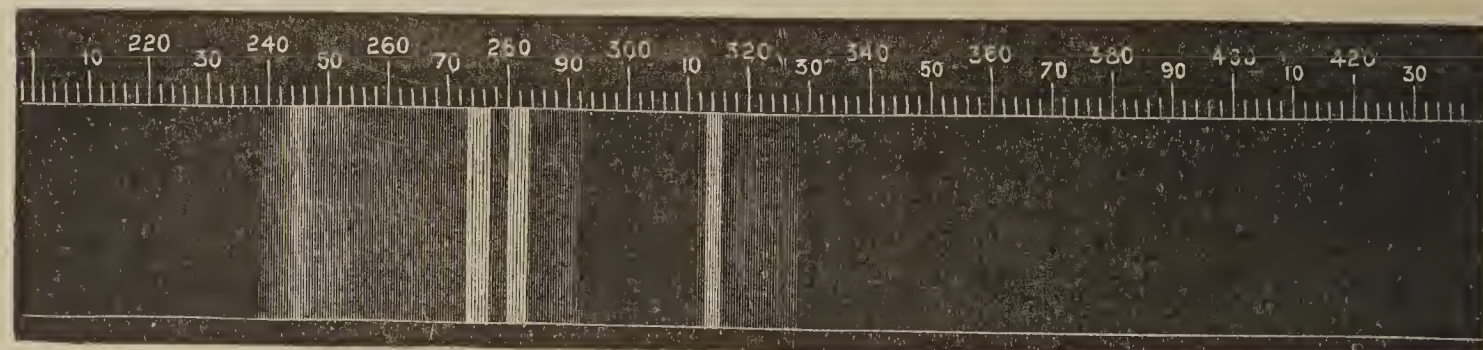
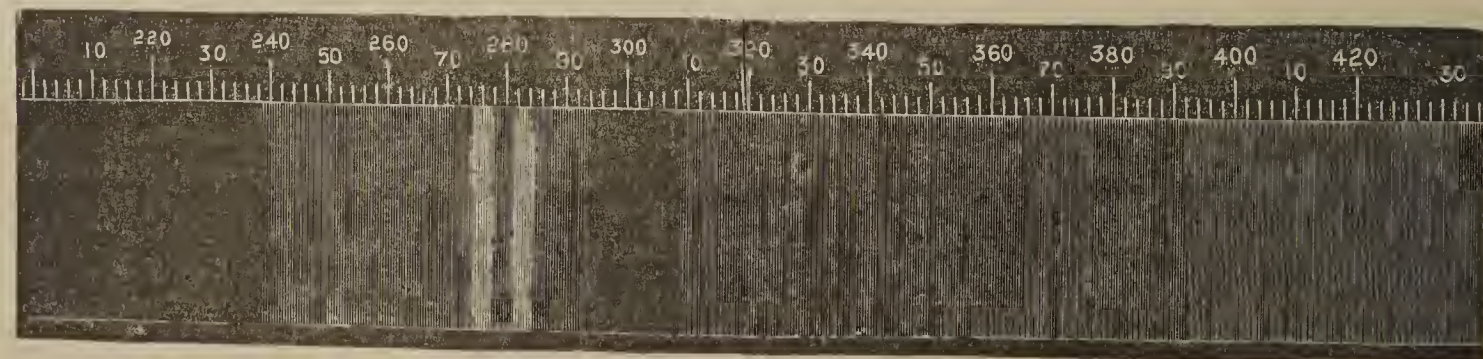


FIG. 18.



of getting some approach to a quantitative estimate of how small a quantity of samarium could be detected.

A solution of specially purified calcic nitrate (79), which was found to contain neither yttrium nor samarium by the radiant-matter test, was standardised, so that 1 part of calcium was contained in 50 parts of solution.

157. A standard solution of samaric nitrate was made containing 1 part of samarium in 100,000 parts of solution.

These solutions were mixed in the proportion of 1 part

* A Paper read before the Royal Society, June 18, 1885.

Fig. 17. The bands are now getting fainter, the second green band is fading out, and the continuous spectrum of calcic sulphate is getting brighter.

160. The next mixture tried contained 1 part of samarium in 100,000 parts of calcium. The appearance of the spectrum is shown in Fig. 18. Here the green is almost gone, being overshadowed by the continuous spectrum of calcium which has spread over it. The red band has likewise almost disappeared in the greater brightness of the continuous red of the calcic spectrum. The double orange band is still very prominent, and the black space, 2942, between it and the green is very marked.

161. The next mixture, 1 part of samarium to 500,000 parts of calcium, gives a spectrum which is fainter than the last, but the orange bands are still distinctly visible. The black space between the yellow and green is strongly marked, but narrower than before. Fig. 19 shows the appearance of this spectrum.

162. A mixture of 1 part of samarium in 1,000,000 parts of calcium was next subjected to experiment. In this the samarium spectrum is very feeble, and the orange bands are only to be seen with difficulty. Now the most striking characteristic of this spectrum is the black space

164. Finally the calcium spectrum by itself was examined. It is continuous, with no break, lines, or bands in it.

The Anomalous Line $\frac{I}{\lambda^2}$ 2693.

165. On several occasions I have spoken of an orange line, 2693, which by its brilliancy and sharpness is a prominent object in most of the samarium-yttrium spectra. With samaric sulphate it is exceedingly faint. With samaria containing 5 per cent of yttria it is very little

FIG. 19.

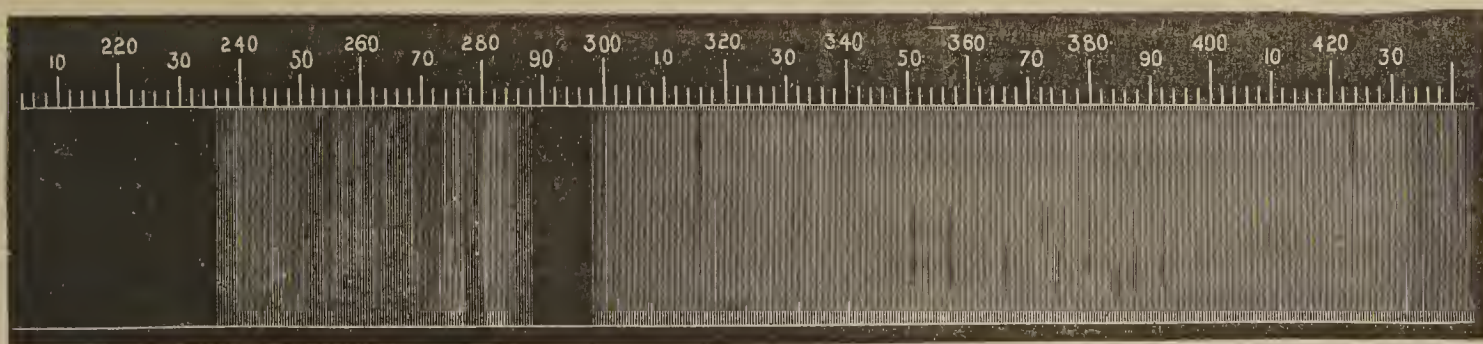


FIG. 20.

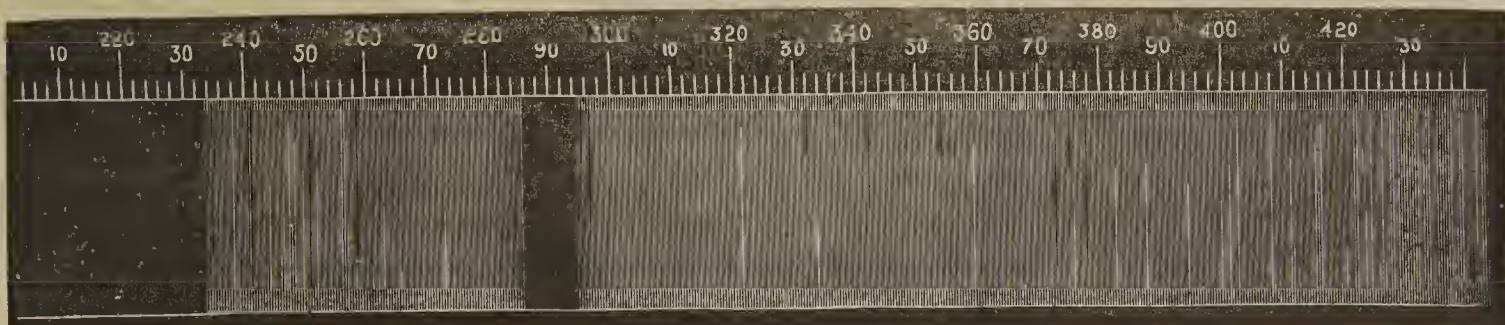


FIG. 21.

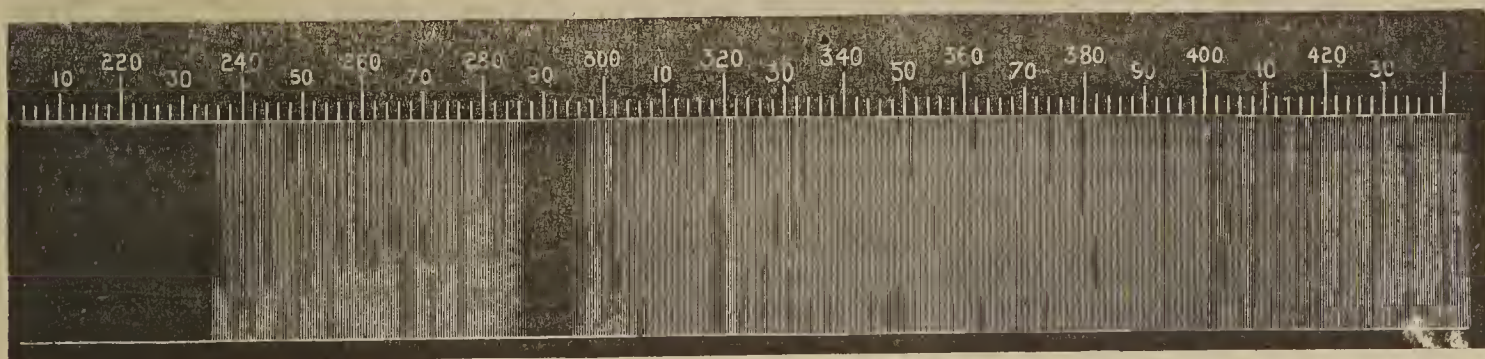
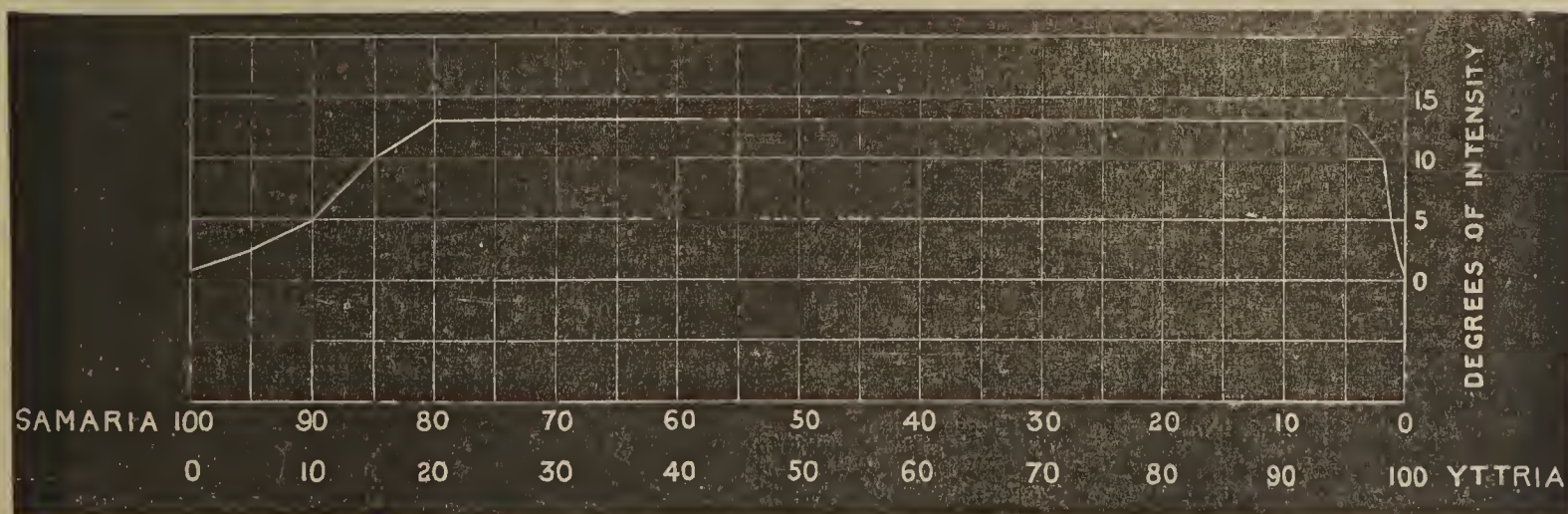


FIG. 22.



which still cuts out the greater portion of the yellow. Fig. 20 represents this spectrum.

163. A mixture of one of samarium in 2,500,000 parts of calcium was now taken. In the spectrum shown by this mixture the bands of samarium have entirely gone, and its presence now is apparent only by the darkening in the yellow portion of what otherwise would be a continuous spectrum. Fig. 21 shows this appearance.

brighter; with 10 per cent of yttria it gains a little; with 15 per cent it is brighter still, and with a mixture of 80 parts samaria and 20 parts yttria it is at its maximum intensity. It continues to be the most striking feature in the spectra of the various mixtures of samaria and yttria until the proportion becomes samaria 3. yttria, 97, when it begins to get less bright, and only when pure yttria is reached does it together vanish.

The accompanying diagram (Fig. 22) shows the rise and fall in intensity of this bright line, with the proportions of samaria and yttria experimented on.

166. It is noteworthy that so long as this bright line is a component of the spectrum, the other bands manifest decidedly less intensity than they do in other phosphorescent spectra where this line is absent. Many of the bands usually present in the samaria and yttria spectra are also suppressed. The profound modification in the spectra of samaria and yttria developed by their mixture is, I believe, without precedent in spectrum analysis. The molecules of each earth, samaria and yttria, which separately are capable of vibrating rhythmically and of giving a characteristic phosphorescent spectrum, when mixed yield a spectrum approaching in character that of samaria or of yttria, according as one or other earth preponderates, and produce the dominant line 2693.

167. In this and the former paper on Radiant Matter Spectroscopy much stress has been laid on the sensitiveness of the Radiant Matter test for indicating the presence of samarium and yttrium; but it might be argued, from the anomalies that arise when *both* these elements occur together, that in reality the Radiant Matter test, however delicate, is not one to be depended upon. For instance, it might reasonably be asked what inference is to be drawn in the case of certain minerals treated with sulphuric acid and tested in the vacuum tube, and found to give only a feeble spectrum? Does this prove the absence of all but traces of either samarium or yttrium, or does it show the presence of both these earths in considerable quantity? The answer is simple. In spite of the perplexing anomalies that have come to light, and are described in this paper, regarding the influence of these two phosphorescing earths on each other, no single instance has occurred during the work connected with this subject in which, with the experience now gained, brilliant phosphorescence and a characteristic spectrum could not be evolved from any mixture containing both or either of the earths samaria and yttria. If, after treatment with sulphuric acid and ignition, the earthy mixture gives a pure spectrum of either yttria or samaria, and the line 2693 is absent, it is pretty safe to assume that the particular earth indicated is alone present. If, however, the spectrum is not quite characteristic, or the anomalous line 2693 is present, it is not sufficient to test the unknown mineral or mixture direct in the vacuum tube. It must first be treated chemically to separate the samaria and yttria (123, 133), and lime must be added before testing in the radiant-matter tube (138), when the spectrum immediately makes its appearance if either of these earths be present in the smallest quantity. Although I say lime is to be added, many other substances perform the same office of eliciting the spectrum, such as baryta, lead, &c. (142—145); but my chief experience has been with lime, and I have always found it to give uniform results under varied conditions.

One important lesson taught by the many anomalies unearthed in these researches is, that inferences drawn from spectrum analysis *per se* are liable to grave doubt, unless at every step the spectroscopist goes hand in hand with the chemist. Spectroscopy may give valuable indications, but chemistry must after all be the court of final appeal.

168. Chemistry, however, by itself would have been helpless to solve the difficulties had it not been possible to appeal at every step to the radiant-matter tube and to the spectroscope. The problems to be solved are so new as to be entirely outside the experience of laboratory work. A double orange-coloured band shows itself in a faint emission spectrum obtained under novel circumstances. On further examination the band, or one not far from it, is seen to occur in minerals of very divergent kinds, and apparently irrespective of their chemical constitution or locality, as well as in laboratory reagents and chemicals of assured purity. This band is sometimes accompanied by bands in other parts of the spectrum, and occasionally shifts its place to the right or to the left. Frequently the

orange band disappears and a citron-coloured band takes its place. Chemical research continued for a longer time than most chemical researches require fails to throw any light on the subject. These being the conditions of the problem, the very last explanation likely to occur to the enquirer would be that these elusive shifting bands were due to the presence of two elements almost universally distributed, and that these two elements should be yttrium and samarium,—yttrium one of the rarest of known elements, and samarium almost unknown at the time its spectrum reaction was first discerned.

VERIFICATION OF THE CALCULATION OF THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 66.)

IV. Analysis of Chlorate of Silver, β 209.

Chlorate of Silver.	Chloride of Silver.	AgClO ₃ : AgCl=100.	Molecular weight of the Chloride of Silver.
138.789 grms.	103.9795 grms.	74.9191 m	143.3808*
259.5287 "	194.4435 "	74.9218 M	143.4011*
Mean, 74.92045			143.39095
Log. = 1.8746003			2.1565218

If p grms. of chlorate of silver gives q grms. of chloride of silver the molecular weight is:—

$$\text{AgCl} = 48 \frac{q}{p - q}$$

The same remark applies to tables VI., VIII., and IX.

V. Synthesis of Bromide of Silver, β 158, 171.

Silver.	Bromide of Silver.	Ag : AgBr=100.	
53.1958 grms.	92.6042	174.0817*	Synthesis by diff.
51.3436 "	89.3780	174.0782* m	Complete syntheses.
55.0615 "	95.8505	174.0790*	
55.8040 "	97.1450	174.0825*	
48.3620 "	84.1904	174.0838* M	
Mean, 174.0810			
Log. = 2.2407515			

In the last four experiments M. Stas also weighed the bromine; the sum of the weights of the bromine and the silver used was 1 m. g. to 10 m. g. higher than the weight of the bromide of silver produced. This follows from the difficulty of freeing bromine of the last traces of humidity. These syntheses by sum are an excellent check, but I have never used them for calculating the mean. M. Stas, on the other hand, only compares the results of the complete syntheses with the conditions necessitated by Prout's hypothesis.

A sixth synthesis is closely related to the 9th determination of the relationship between silver and bromide of potassium, Table VIII.

VI. Analyses of Bromate of Silver, β 200.

Bromate of Silver.	Bromide of Silver.	AgBrO ₃ : AgBr=100.	Molecular weight of Bromide of Silver.
86.5457 grms.	68.9310 grms.	79.6469* m	187.8368
101.9875 "	81.2361 "	79.6530 M	187.9069
Mean, 79.6500			187.8718
Log. = 1.9011856			2.2738617

* Ann. Chim. Phys., 6th Series, vol. vii., April, 1886.

VII. Synthesis of Iodide of Silver, β 135, 152.

AgI : Ag=100.

Silver.	Iodide of Silver.	Sum of the Iodine and Silver used.	By the Silver Iodide obtained.	By the weights of Iodine and Silver used.
Grms.	Grms.	Grms.		
97.5915	212.2905	Syntheses by diff.	217.5297*	—
43.5281	94.6894*		217.5362	—
27.6223	60.0860	60.0888	217.5271 m	217.5373*
39.8405	86.6653	86.6687	217.5306	217.5392*
24.4649	Not obtained.	53.2201	—	217.5366*
38.0795	82.8375	82.8394	217.5383	217.5433 M
136.3547	296.6240	296.6299	217.5385	217.5429*
82.33735	179.1080*	179.10745*	217.5294	217.5287*

Mean, 217.5328 217.5380

Mean of thirteen estimations, 217.5352

Log. = 2.3375295

In the last experiment the figures in M. Stas's table do not agree with the details β 148—150. The weight of silver I used is the first weight, 82.3231 grm., plus that used for precipitating the iodine in the liquid (1098.9 c.c. or 1104.9 c.c.) which remained with the iodide of silver = 0.013 grm. + that used to ensure accuracy = 0.00125 grm. The weight of the iodine is the original weight, 96.7964 grms. + that used to ensure accuracy = 0.0013 grm., minus the iodine taken up by the 2019.7 c.c. of liquid = 0.0276* grm.

The oxide of potassium could not hold more than 3 m.g. of water. The water taken up diminishes the molecular weight.

In the *second series* the chlorate was decomposed by hydrochloric acid. The two methods reversing the errors, I consider the mean of the second series as the most probable figure, see γ 59.

Chlorate of Potash.	Oxygen.	KClO ₃ : 3O=100.	Molecular Weight of Chloride of Potassium.
69.8730 grms.	27.3636 grms.	39.1619 M	74.5681 m
82.1260 "	32.1612 "	39.1608*	74.5716
86.5010 "	33.8706*	39.1563*	74.5856
132.9230 "	52.0426*	39.1524*	74.5977
127.2125 "	49.8102 "	39.1551	74.5893
59.727 "	23.3830 "	39.1498	74.6060
95.7975 "	37.5020 "	39.1472 m	74.6143 M
147.318 "	57.6840 "	39.1561	74.5862

Mean of eight estimations = 39.1549* 74.5898
Log. = 1.5927861 1.8726794

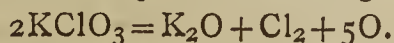
Mean of the 2nd series = 39.1510 74.6022
Log. = 1.5927429 1.8727517

(To be continued).

Iodate of Silver.	Iodide of Silver.	Oxygen.	AgIO ₃ : AgI=100 after the weights of Iodide of Silver.	Molecular weights of Iodide of Silver according to the weights	
				of the Iodide used.	of the oxygen set free.
98.2681 grms.	81.5880 grms.	16.6815*	83.0259*	234.7842*	234.7645
156.7859 „	130.1755 „	26.6084	83.0276 M	234.8114	234.8290
76.5561 „	63.5600 „	Synthesis by diff.	83.0241 <i>m</i>	234.7535*	—
			Mean = 83.0259	234.7830	234.79675
			Log. = 1.9192136	Mean of five estimations, 234.7885	
				Log. = 2.3706768	

IX. Analysis of Chlorate of Potassium, α 320, 321.

In the *first series* the chlorate was decomposed by heat. A small portion is decomposed according to the equation—



Instead of one atom of oxygen = 16, two atoms of chlorine = 70.912 are set free. The loss of weight of the chlorate is thus too great in the relation of 54.912 to 70.912 of chlorine set free. This chlorine was absorbed in a tube containing finely divided silver heated to a dull red colour.*

For the five experiments the weight of this chlorine reached—

7.5 m.g. 11.0 m.g. 2.5 m.g. 8.5 m.g. and 3.6 m.g.

It was therefore necessary to reduce the apparent weight of the oxygen.

5.81* m.g. 8.52 m.g. 1.94* m.g. 6.58* m.g. and 2.79 m.g.

M. Stas believes that traces of chlorine were still carried over without uniting with the silver.

The chlorate of potash contained at least 5.100000 of silica (α 258, 309; β 233), which causes the molecular weight of the chloride of potassium to be put too high. On the other hand, a very small quantity of water was given off by the sulphuric acid tubes (not more than 4 m.g.).

* According to M. Schützenberger oxygen has the power, in the cold, of putting chlorine into a mysterious state so that it will not precipitate the salts of silver (*Comptes Rendus de l'Académie des Sciences*, xcvi, p. 1520, 1884).

ON THE PREPARATION OF TRICHLORMETHYL-SULPHONIC CHLORIDE.

By H. BASSETT.

HAVING had occasion to prepare some of this substance, after making trial of the method of Berzelius and Marcet, its discoverers, and also of that recommended by Kolbe, I devised the following process, which is most satisfactory from its facility and economy.

Take potassium chlorate in powder 100 grms., add to this, in a flask, a mixture of 200 c.c. common hydrochloric acid and 400 c.c. water, and then 50 c.c. bisulphide of carbon, and leave the flask loosely covered with a small inverted beaker, preferably outside a window in a good light. In an hour or so the action commences; the liquid turns yellow, and minute bubbles of gas disengage themselves from the bisulphide of carbon. Strong sunlight may cause the flask to become hot, in which case the reaction becomes too violent, and must be moderated by cooling under the tap. In the heat of summer the proportion of water should be increased, but in frosty weather with no sun equal volumes of acid and water may be used.

The action goes on without requiring any particular attention beyond occasional agitation till finished, which may take from three days to a fortnight, according to the light, &c. The completion of the action is well

marked; the chlorate is completely dissolved in the clear yellow solution; the bisulphide, which has gradually become thick and pasty, is converted into the white solid product, and the evolution of gas which has continued throughout the reaction completely ceases. It is then only necessary to pour off the strongly acid liquid, wash well with water, after crushing the peculiarly tough lumps in a mortar, and then wash thoroughly free from acid on a linen filter. The mass is then squeezed as dry as possible in the cloth, broken or crumbled up, and dried over sulphuric acid till it ceases to lose weight.

Two reactions appear to go on together, one portion of the bisulphide being entirely converted into carbonic and sulphuric acids, and the yield of trichlormethylsulphonic chloride varies in different experiments, being greater when the action is slower, from cold weather, &c. I have obtained 43 grms. as a maximum from 50 c.c. bisulphide of carbon.

The product obtained as above is quite white and clean, and when sublimed leaves only a very small residue of impurities. The bottles containing it become after a time coated with very beautiful lustrous transparent crystals, having the melting-point, 135° , attributed to the pure substance.

NEW EXPERIMENTS ON THE DECOMPOSITION OF HYDROFLUORIC ACID BY AN ELECTRICAL CURRENT.

By H. MOISSAN.

IN decomposing, by an electric current, hydrofluoric acid rendered conductive by means of a hydrofluoride of potassium fluoride, we obtain at the positive pole a gaseous body having very energetic properties, and which, according to former researches, must be either fluorine or hydrogen perfluoride.

The author now indicates a new process for preparing this gas, founded on the electrolysis of the hydrofluoride of potassium fluoride, carefully dried and kept in fusion at the temperature of 110° . The experiment is made in the apparatus formerly described. The melted hydrofluoride swells up much under the action of the current, a portion escapes by the abductor-tubes, and at this temperature of 110° the platinum was so strongly attacked that the experiment could not be continued. If platinum wires conveying the current of ten Bunsen elements are plunged to the hydrofluoride kept in a liquid state in a platinum capsule, gases are evolved in abundance at each pole, and when they come in contact they produce—even in the dark—a slight detonation. The platinum wires are corroded in a few moments.

It must be added that in the electrolysis of hydrofluoric acid there may be obtained at each pole a yield of $1\frac{1}{2}$ to 2 litres per hour, whilst the experiment may easily be continued for three hours if we employ a sufficient quantity of hydrofluoric acid. Is the gas thus obtained a compound of hydrogen and of fluorine more highly fluorised than hydrofluoric acid? Are we not in presence of hydrogen perfluoride? To answer this question it is sufficient to show that the gas thus obtained contains no hydrogen. This may be done by passing the gas over iron kept at a red-heat. In case of fluorine the gas should be entirely absorbed; if, on the contrary, we have obtained a compound of fluorine and hydrogen, this latter gas will be set at liberty, and might be collected in an atmosphere of carbonic acid, from which it may be easily freed by means of a solution of potassa.

The experiment was arranged as follows:—At the end of the platinum tube at which the active gas is liberated is placed a tube of the same metal, one-fifth of a metre in length, filled with fragments of potassium fluoride absolutely dry. This compound retains very well the vapours of hydrofluoric acid which escape simultaneously. A

potash tube of the same length adjusted to the former contains a bundle of iron wires, and has been tared before the experiment. To this last metallic tube is connected, by means of a caoutchouc joint, a large test-tube, and then a bottle, both inverted and filled with pure carbonic acid. This part of the apparatus was traversed before the experiment by a rapid current of pure, dry, carbonic acid. The gas escaping was analysed: 100 c.c., after absorption by carbon dioxide, left merely a very small bubble of air, the volume of which was unimportant. On the hydrogen side were arranged a test-tube and a 1-litre bottle, connected by bent tubes and likewise full of pure carbonic acid. The extremity of each apparatus is in communication with the air by means of a caoutchouc tube, 2 metres in length, the open end of which is raised and placed above the level of the carbonic acid in the bottles. By this arrangement it was possible to collect separately and without pressure the gases escaping from the platinum apparatus, both at the negative and the positive poles. After all these precautions were taken the current of twenty Bunsen elements was passed into the hydrofluoric acid, which was surrounded by methyl chloride and cooled to -50 by a rapid current of air. The platinum tube containing the iron is heated at once to dull redness, and there can be remarked the form of the iron wires burning in the gas. The electrolytic decomposition is allowed to go on for ten minutes, replacing the methylchloride if requisite. The experiment is then stopped, the apparatus taken down, and the tube containing the iron fluoride is weighed. It is found as a crystalline fluoride, of a white colour, slightly greenish, at the end of the iron wires; there is also a small quantity of platinum fluoride. The apparatus filled with carbonic acid is transferred to a water-trough, and slowly absorbed by a solution of potassa. The remaining gas is measured and analysed. The weight of the iron was increased by 0.130 grm.; the gas coming from the negative pole contained 78 c.c. of hydrogen, burning with a pale flame without detonation. The active gas, deprived of hydrofluoric acid by means of potassium fluoride, had thus been entirely absorbed by iron raised to dull redness, yielding a weight of iron fluoride sensibly corresponding to the weight of the hydrogen liberated. The gas which electrolysis liberates from anhydrous hydrofluoric acid, or from the hydrofluorised fluoride, is therefore fluorine.—*Comptes Rendus*, ciii., p. 256.

ON THE DETERMINATION OF ABSOLUTE NEUTRALITY.

By J. R. DUGGAN.

(Concluded from page 69).

IF, now, formic acid is used instead of acetic, a similar series is obtained, except that the retardation from the normal salt is not so great, and the excess of acid required to prevent retardation is considerably less. With propionic acid the reverse is the case, the retardation from the normal salt being greater, and more than two equivalents of acid to one of base being necessary to prevent retardation. It is evident from this that in sodium formate the alkali is more nearly neutralised than in the acetate, while it is less so in the propionate. It will be seen from this that this reaction can be utilised to determine the power that different acids have for neutralising an alkali. Instead of determining the excess of acid which was necessary to neutralise the normal salt, it was found that more accurate results could be obtained, without affecting the proportion, by finding the amount required to retard the reaction 50 per cent. As a standard for comparison a flask containing five equivalents of acetic to one of sodium acetate was used, instead of one containing only diastase and starch. This retarded about 50 per cent, but as

it was desirable simply to compare the acids among themselves, the actual degree of retardation was of little importance. The amounts of various acids in excess of the one equivalent which combined with the caustic soda to form the normal salt, which were necessary to produce the same retardation as the five equivalents of acetic, are given in the first column of Table III. They are for convenience expressed in their caustic soda equivalents in the second column. The figures are the amounts required with 20 m.grms. of caustic soda, as this was the amount generally used, but in some of the series 40 m.grms. were used. The results are the mean of several series.

TABLE III.

Acid.	Required amount.	NaOH Equivalent.
Formic	14.4 m.grms.	12.5 m.grms.
Acetic	150	100
Propionic	246	133
Isobutyric	273	124
Lactic	27.0	12.0
Benzoic	82.4	27.0
Phenylacetic ..	129	38.0
Oxalic	6.30	5.60
Succinic	109	74.0
Pyrotartaric ..	99.0	60.0
Malic	38.5	23.0
Tartaric	18.4	9.80
Fumaric	18.3	12.6
Phthalic 1:2 ..	42.5	20.5
Citric	46.4	29.0

These figures represent the amount of each acid necessary to produce a certain degree of acidity in a solution which contains the amount of salt formed by the combination of the acid with 20 m.grms. of caustic soda. Of course the affinity of each of the acids is less than that of caustic soda. If acids having a coefficient of affinity greater than that of the base were used, it would then become necessary to use a certain amount of some alkali to prevent the retardation caused by the normal salt, since it would be acid. This part of the subject has not yet been investigated, except to a very slight extent.

The neutralisation of an alkaline base by an acid of lower affinity may be divided into two stages—the saturation of the base to form a normal salt and the neutralisation of the alkaline salt. The amount of acid necessary to accomplish the first of these depends, of course, upon its combining weight and the number of replaceable hydrogen atoms it contains. In order to determine if the amount required in the second stage depends upon the affinity of the acid, the following experiments were made. Since, according to Ostwald,* the power which an acid shows in inverting cane-sugar is the most reliable measure of its affinity, I determined the amount of each of the acids that is required to convert a given amount of cane-sugar under fixed conditions. 10 c.c. of a 20 per cent solution of cane-sugar was, in each case, made up to 50 c.c. by the addition of the acid and water. The solutions were heated to 70° C. before mixing, and kept in a water-bath at this temperature for thirty minutes. The reaction was stopped by the addition of a slight excess of caustic soda, and the sugar determined by Fehling's solution as dextrose. The standard for comparison was in each case a flask containing the above amount of sugar and 0.150 gm. of acetic acid. By using this as a control experiment, any slight variation in time or temperature caused no error, as all the flasks were under the same conditions. The first column in Table IV. shows the amount of each acid required to produce the same amount of conversion as 0.150 gm. of acetic. In the second column the acids are expressed in their soda equivalents, while the third is a repetition, for comparison, of the second column of Table III. The fourth column gives the percentage proportion between the figures in the

second and third columns, those in the second being taken as 100.

TABLE IV.

Acid.	Inversion of Cane-sugar.		NaOH equiv. of amount required to neutralise the normal salt.	Per cent proportion.
	Required amount.	NaOH equiv.		
	M.grms.	M.grms.	M.grms.	
<i>Monobasic.</i>				
Formic	13.8	12.0	12.5	104
Acetic	150	100	100	100
Propionic	255	138	133	96.4
Isobutyric	286	130	124	95.4
Lactic	26.1	11.6	12.0	103
Benzoic	85.0	27.9	27.0	96.4
Phenylacetic ..	125	37.3	38.0	102
<i>Dibasic.</i>				
Oxalic	3.71	3.30	5.60	169
Succinic	66.4	45.0	74.0	164
Pyrotartaric ..	57.8	35.0	60.0	171
Malic	20.8	12.4	23.0	(185)
Tartaric	10.9	5.80	9.80	169
Fumaric	10.9	7.50	12.6	163
Phthalic 1:2 ..	11.6	5.60	20.5	366
<i>Tribasic.</i>				
Citric	15.7	9.80	29.0	296

It is evident from this table that the amount of a monobasic acid required to neutralise an alkaline salt of that acid is proportional to its affinity as measured by its action on cane-sugar. Spohr has reached practically the same conclusion from his study of the influence of normal salts on the inversion of cane-sugar by acids.* In the case of dibasic acids the table shows that more is required to neutralise the salt than with monobasic acids, or that the normal salt is more alkaline than it would be if formed from a monobasic acid of the same affinity-constant. For example, it was found that normal sodium succinate retards the action of diastase more than an equivalent quantity of sodium acetate, although succinic acid inverts sugar more rapidly than acetic, and might therefore be supposed to form a less alkaline salt. It must be remembered that in comparing the action of acids, the carboxyl groups are compared, so that half an equivalent is used in the case of dibasic acids. To explain this greater alkalinity of salts of dibasic acids, we must suppose that each atom of sodium not only neutralises the carboxyl group into which it enters, but influences in some manner the other similar group in the molecule. There is reason to suppose that a molecule of oxalic acid inverts cane-sugar more rapidly than would two molecules of an acid having the formula COOH, or that the affinity of polybasic acids is increased by a mutual reaction between the carboxyl groups.† This being true, it follows that the neutralisation of one carboxyl group in such an acid must diminish the affinity of the remaining ones. In the case of phthalic acid this action is much more marked than with acids of the paraffin series. This cannot be due to experimental error, as this acid was examined very carefully; but it will be necessary to examine other acids in which we have what is termed the ring structure before attempting any explanation of this. In the case of the one tribasic acid examined, the amount of acid required to neutralise the salt is, as would be supposed, more than with either mono- or dibasic. As all of these results were obtained from the use of a monacid base, it does not follow that they would hold good for a polyacid base.

The greater alkalinity of salts of polybasic acids is very well shown in the case of phosphoric acid, for although a molecule of this acid converts sugar more rapidly than three molecules of acetic, it is with considerable difficulty that the acid can be made to form a normal sodium salt. In other words, the acidity of the acid is so well neutralised by one or two atoms of sodium that it is only with

* Loc. cit.

* Jour. f. prak. Chem., (2), xxxii., 46.

† See Muir's Principles of Chemistry, p. 470.

difficulty that it can hold a third. The reverse of this tendency of the weaker polybasic acids to form only primary or secondary salts is seen in the frequent formation of basic salts when a strong acid combines with a slightly alkaline base.

The Influence of Alcohols on Diastatic Action.

In the presence of about 7 p.c. by weight of ethyl alcohol the action of diastase is retarded one-half, but if there is added to 100 c.c. of the solution about 3 m.grms. of acetic acid there is but little retardation. That the retardation by the alcohol which is prevented by this minute quantity of acid is due to its alkalinity is borne out by the fact that the inversion of cane-sugar by acids is also retarded by the presence of alcohol. Titration before and after the experiment showed that there was no etherification, as would be supposed, considering the extreme dilution of the acid. It seems natural to conclude from this that there is here a condition similar to a basic salt in which a great many molecules of the base are combined with one of acid, for if such is not the case, it is difficult to explain the action of the acid in neutralising the alcohol. Under these conditions the alcohol shows alkaline, but not basic properties, since it does not unite with the acid to form an ester (salt). This action of alcohols is of considerable physiological interest, and I hope by further study to throw some light on their action on the living organism. As we approach the acid-phenols through the secondary and tertiary alcohols we find that they act less and less on diastase, until phenol is reached, when we get decided action from its acidity. I hope to verify the results I have obtained by a further study of the influence of alcohols on the inversion of cane-sugar by acids, and until that is done, a lengthy discussion including the different alcohols would be premature.

As the value of any method depends to a great extent upon its accuracy, it will be well to notice the experimental errors that show themselves in the above determinations. An examination of the fourth column of Table IV. shows that these may amount to several per cent. Of course, any impurity in the acid is likely to produce an error, and this is probably the cause of the rather larger amount of malic acid required to neutralise the normal salt. In the experiments with diastase there is probably a small amount of the acid used up in combining with the proteid matter and salts which cannot be entirely removed from the starch and diastase solution. It will be seen that rather more of the acids which have a high affinity constant is required than the theory calls for. As they are used in small amounts, any proteid matter present would render inactive a proportionately larger quantity of these than of the weaker acids. Ostwald has shown that the results obtained from the inversion of cane-sugar depend to a slight extent on the concentration of the solutions used. When the errors from these and other causes happen to be all on the same side, it is not surprising that they should amount to several per cent. I think the results obtained, however, show that the method is valuable, and will assist in the important work that Ostwald has undertaken. It cannot be doubted that the physiological action of organic acids is dependent to a great extent on their affinity, and the determination of affinity-constants will probably be of as much value to physiological as to pure chemistry.

In conclusion, I do not think it will be out of place to offer a protest against the custom of calling salts acid or neutral according to whether a part or all of the hydrogen is replaced. Primary or mono-sodium carbonate is not an acid salt, nor is the normal salt neutral. This is an extreme case, but it is taken to show that such a use of these terms is incorrect even if we use only the ordinary colour indicators.

I am under many obligations to Prof. Remsen for suggestions and for advice which he has kindly given me during the progress of the work.—*American Chemical Journal*.

NOTICES OF BOOKS.

The Chemistry of Wheat, Flour, and Bread, and Technology of Bread-Making. By W. JAGO, F.C.S., F.I.C.

THE chemistry of flour and bread, notwithstanding its obvious importance, is overlooked or but slightly touched upon in technological cyclopædias. Hence there is fair room for the very comprehensive treatise which Mr. Jago here lays before the public. The foundations of the work are, as here stated, a paper on the same subject read before the National Association of British and Irish Millers in 1883, and a course of sixty-four articles which subsequently appeared in the *Millers' Gazette*. These papers have been elaborated into the volume before us.

The author sets out with three chapters on general chemistry. The fourth chapter is devoted to the microscope and the polarisation of light. All these chapters are well written, but it is at least an open question whether the reader might not, for all the information they contain, have been referred to some one or other of the many chemical manuals which are now so plentiful. The only two points in these chapters calling for remark are the use, in one instance, of the unhappy term "metalloids" for the non-metallic elements, and the description of methylated spirit given on p. 39, which is decidedly too favourable. As ordinarily to be bought it contains shellac, and is thus rendered ill-fitted for almost every conceivable operation except the production of varnishes. Even when free from shellac the aldehyd and other impurities present in the raw wood-spirit grievously interfere with its uses both in research and in the chemical arts.

With Chapter 5 begins what may be called the special portion of the work. We have here an account of the carbohydrates and their transformations, of the albumenoids, of fermentation, of the lactic and putrescent fermentations, &c.; the paragraphs on yeast as an organism, on its botanic position, its varieties, and its life-history. The chemical distinctions which the author draws between plants and animals seem to us too absolute. The carnivorous plants, far more numerous than it was long supposed, nourish themselves in part from complex organic matter. Vegetables are also known which in certain phases of their existence normally evolve heat. On the other hand, chlorophyll, with its function of decomposing carbon dioxide, has been traced in the animal world, and among the great group of arthropods synthesis is a prominent function.

In the chapter on the manufacture and strength of yeasts the author fails to show how the terms yeast and barm replace each other in different parts of the kingdom. In Cheshire, Lancashire, and the south-west of Yorkshire, the product derived from the brewery is invariably known as barm. In the South of England and in the more northern parts of Yorkshire, from about Huddersfield onwards, the word "yeast" is universal, and to most of the inhabitants "barm" is unintelligible.

From Chapter 13 the author proceeds to Moulds and Fungoid Growths of the Physical and Chemical Composition of Wheat. Here we find some very valuable tables showing the analysis of the grain from the principal wheat-growing districts. Bread-making is discussed at length. Here the judicious rule is laid down that a water unfit for drinking is also unfit for baking. Living organisms, it is shown, are liable to set up putrefactive fermentations. The sanitary aspects are next considered. These, it is well known, are far from faultless, especially in London. Several kneading-machines are mentioned, and it is much to be desired that bread should be untouched by hand in every stage of its preparation. Baking powders containing potassium bisulphate and alum are deservedly condemned. The use of hydrochloric acid and sodium carbonate for raising bread is objected to, as the acid of commerce generally contains arsenic.

The "bread-reform" movement does not meet with

approbation. It is shown that the retention of bran in the flour irritates the intestine, quickens the peristaltic action, and thus hinders the complete digestion of the albumenoids present.

The remainder of the work deals chiefly with the analysis of wheats, flours, and bread. Here we find that the determination of albumenoids by the ammonia process, as invented by Wanklyn and Chapman, is given at considerable length. Strong exception is taken to the opinion of Wanklyn and Cooper ("Bread Analysis") as to the quantity of water which bread may legitimately contain.

Taking Mr. Jago's work as a whole it deserves a welcome as supplying a distinct want in our technical literature.

Two clerical errors are frequently repeated: phenolphthaleine is printed phenolphthalien, and the name Soxhlet is converted into Soxhlett. A very disagreeable feature is the introduction of two pages of advertisements in the middle of the book,—an innovation which we hope may not find imitators. The work, it must be added, is not published through the trade, and can be obtained only direct from the author.

CORRESPONDENCE.

FUCHSINE—PYROXYLIN—PHYLLOXERA.

To the Editor of the Chemical News.

SIR,—I notice in the CHEMICAL NEWS (vol. liv., p. 46), in a review of Professor Edgar Smith's translation of Von Richter's "Chemistry of the Carbon Compounds," your reviewer protests against the use of the name "fuchsine" as descriptive of the commercial salts of rosaniline, preferring they should be called "magenta," on the ground that "fuchsine" is a name "unpronounceable by every Englishman who is not a German scholar." The same objection to the name fuchsine was made in the review in these pages (July 3rd, 1885) of Vol. I. of my own work on "Commercial Organic Analysis," but I did not then feel justified in making the protest which I can now that the criticism is applied to the work of another writer. It seems to me that the Reviewer's objection to the term "fuchsine" is a mistaken one. The name appears to me eminently applicable to a colouring matter capable of dyeing goods a tint closely resembling that of the flower called a "fuchsia," which word is well-known to every Englishman, and the common pronunciation of it corresponds with that I find attributed to it in Nuttall's "Dictionary," which is "few'-she-a." On the other hand, your reviewer prefers the word "magenta," a name which is not descriptive, and which seems to me less suitable than that of "fuchsine."

While on the subject, I may mention another word which, to my mind, is frequently mispronounced, and that is "pyroxylin." There are no two opinions as to the way in which xylene and para-xylene should be pronounced, and surely pyro-xyl-in should be treated similarly. Yet how often do we hear chemists, who consider themselves men of light and leading, pronounce pyroxylin in a manner parallel to hydroxyl. Are they right, or am I, and is it phyllox-era (fylocksera) or phyllo-xera (fyloxera).—I am, &c.,

ALFRED H. ALLEN.

RADICAL OR RADICLE?

To the Editor of the Chemical News.

SIR,—The letter which Dr. Divers addressed to you (CHEMICAL NEWS, vol. liv., p. 36) as a protest against what he holds to be the incorrect mode of spelling adopted by the Editor and Publication Committee of the Chemical Society, reminds me of the discussion started twenty-

two years ago in the correspondence columns of the CHEMICAL NEWS (vol. ix., pp. 143, 166, 191, &c.).

In the year 1864 the transition from *radical* to *radicle* was beginning to find favour, owing, perhaps, to the then recent appearance of the article on Acetyl in "Watts's Dictionary," and, under my initials J. S., I wrote you a couple of letters showing that, out of forty-nine communications examined, the authors, commencing with Hofmann and Brodie, had in thirty-three instances followed the old style of spelling, whilst only sixteen adopted the new word "radicle." You were then with me (see Editorial Note, p. 167) in advocating the retention of the old word, for which Dr. Divers now pleads.

The learned professor will see his manuscript altered in the current *Journal of the Chemical Society* (Divers and Shimidzu on "Mercury Sulphites and the Constitution of Sulphites"), printed copy of which cannot yet have reached him in Japan, and the spelling throughout made to accord with Prof. G. C. Foster's article on Radicles in "Watts's Dictionary," or rather with the Society's editorial dictum.

I submit that the arguments adduced by Dr. Divers in his recent letter to you are unanswerable, or at least have not been met by Mr. Madan in his last week's reply.—I am, &c.,

JOHN SPILLER.

London, August 10, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 4, July 26, 1886.

Determination of Ammonia.—Th. Schlœsing.—Calcined magnesia is constantly used in agricultural laboratories to displace ammonia from its saline combinations and to permit its extraction by distillation and its volumetric determination. Its use has been especially recommended by M. Boussingault, after careful study, for determining ammonia in presence of nitrogenised organic substances, and recommendations have been reproduced by M. Peligot and M. Grandeau in their treatises of agricultural chemistry. If magnesia does not permit the extraction of the totality of the ammonia from dissolved magnesian salts, it must be admitted that the authors just mentioned have adopted a quite insufficient method for determining one of the most important substances in agriculture. The scientific labours of M. Boussingault on the ammonia contained in organic substances and the results obtained by the author in his researches on atmospheric ammonia will be gravely compromised. It is only after the most careful verification that he has adopted a process founded on distillation in presence of magnesia for the determination of ammonia. M. Schlœsing then recounts his recent experiments, the results of which do not agree with the conclusions of MM. Berthelot and André.

Slow Decomposition of the Chlorides in their Dilute Solutions.—G. Foussereau.—In a former paper the author has the results of a study on the decomposition of ferric chloride by water observed by means of the variations of electric resistance. He has now extended his observations to the aluminium, magnesium, double rhodium, and sodium, platinum, and gold chlorides.

New Experiments on the Electrolysis of Hydrofluoric Acid.—H. Moissan.—(See p. 80).

Separation of Antimony and Tin.—Ad. Carnot.—This paper also will appear in full.

Numerical Laws of Chemical Equilibria.—H. Le Chatelier.—A mathematical paper not susceptible of useful abstraction.

On the Sodium Manganites.—G. Rousseau.—Manganese chloride introduced in small quantities into an alkaline earthy oxychloride kept in fusion in contact with the air is quickly transformed into manganate. On prolonged heating the manganate is dissociated, forming manganites whose complexity varies with the temperature. The author has succeeded in producing two varieties of sodium manganite by the following process:—3 grms. caustic soda are melted in a platinum crucible over a Bunsen burner; 1.5 grms. dried manganese chloride is added, and there are lastly introduced 3 grms. sodium nitrate. The mixture is kept in fusion at dark redness, constantly stirring. When the greater part of the sodium nitrate is decomposed the temperature is raised to the volatilisation point of potassa and the heat is continued for about four hours, leaving the crucible uncovered.

Determination of the Absolute Acidity of the Organism and on Certain Phenomena Relating to the Saturation of Orthophosphoric Acid.—Ch. Blarez.—The exact determination of the absolute basicity of phosphoric acid is not possible, since this basicity is not absolute; a molecule of acid may, according to circumstances, unite not only with one or two mols. of base to form definite salts, but also with a larger quantity. As phosphoric acid and the phosphates form part of the constituent principles of animal liquids it is impossible to determine the absolute acidity of these liquids in presence of a body requiring a variable quantity of base for their theoretical neutralisation.

Certain Thermic Data Concerning the Chromates.—Paul Sabatier.

Thermic Researches on the Selenides.—Charles Fabre.—For the results of these two papers we must refer to the original.

Researches on Certain Crystalline Basic Sulphates.—M. Athanasesco.—By means of Friedel's process the author has obtained well-crystallised basic sulphates of cadmium, zinc, aluminium, iron and aluminium, and, by a slightly modified process he has formed basic sulphates of nickel, cobalt, mercury, and bismuth. All these bodies are insoluble in and undecomposable by water; aluminium sub-sulphate is insoluble even in boiling acids. All except that of mercury contain water which, in the majority of cases, is eliminated only at very high temperatures, sometimes above 300°, and is probably, therefore, combined water.

Researches on Certain Crystalline Arseniates.—M. Coloriano.—All these arseniates, except the bibasic ones are insoluble in water and are not readily attacked by acids. The hydrated basic acids retain their water up to a very high temperature.

A Nitro-Camphor and on its Saline and Alcoholic Combinations.—P. Cazeneuve.—On treating normal chloronitrous camphor by zinc, copper, iron, or alkalies in presence of dilute alcohol it is decomposed with formation of a metallic chloride and oxide or an alkaline chloride or chlorate, whilst there is formed a true salt of nitro-camphor united with the metal in question.

Discussion of the Reactions of Pilocarpine.—E. Hardy and G. Calmels.—This memoir does not admit of useful abridgment.

Physiological Function of the Pulmonary Tissue in the Exhalation of Carbonic Acid.—L. Garnier.—There exists in the pulmonary tissue a body of an acid function distinct from taurine. Whether or not this body is Verdeil's "pneumic acid" the fact of the acidity of the lungs is in itself of great physiological importance.

Chromatometer for Measuring the Colour of Liquids.—L. Andrien (de l'Etang).—This paper requires the accompanying illustration.

Zeitschrift für Analytische Chemie.

Vol. xxv., Part 3, 1886.

Applicability of Malleable Nickel for Chemical Apparatus.—Fr. Stolba.—Noticed some time ago.

Organic Impurities in Hydrochloric Acid.—F. Schröder.—The acid in question is obtained as a by-product in the manufacture of certain organic substances and can generally be detected by its odour. Such acid is inadmissible for scientific and for pharmaceutical purposes.

Neutral Litmus Paper.—K. Mays.—100 grms. of litmus, without pulverising, are boiled in 700 c.c. of water, which is then poured off, and the residue is again boiled up with 300 c.c. of water. The mixed extracts are allowed to settle for one to two days, acidulated with hydrochloric acid and dialysed in a current for 8 days. Unsized paper is then prepared in the ordinary manner with this neutral solution of litmus.

Electrolytic Separation of Metals.—M. Kilian.—From solutions containing salts of various metals the metals may be completely and successively separated in a state of purity by using currents of different strengths. The current first applied must be only sufficient to throw down the most readily precipitable metal, but not the next following. The more of this first metal is deposited the feebler becomes the current, and finally a galvanometer introduced into the circuit is no longer affected; a sign that now none of the metal precipitable by the existing electromotive power is present, but only such saline solutions as do not conduct the feeble current and consequently are not decomposed. If the negative electrode is charged and the electromotive power increased a second metal can be precipitated.

Electrolytic Separation of Molybdenum.—E. F. Smith and W. S. Hoskinson.—From the *American Chemical Journal*.

Electrolytic Determination of Mercury.—Luis de la Escosura and Horacio Bentabol y Ureta.—The author's process has been already inserted. Prof. Classen writes that he communicated this process to Don L. de la Escosura two years ago, whilst Don H. Bentabol y Ureta's memoir bears date January 15th of the present year.

A New Method for Separating Iron and Alumina.—M. Flinski and G. von Knorre.—This paper will be inserted in full.

A New Method for the Determination of Cadmium.—Ad. Carnot and P. M. Proromont.—Inserted from the *Comptes Rendus*.

Determination of Arsenic.—F. Reich and Th. Richter.—This method has been discussed in the *CHEMICAL NEWS* by Leroy McCay, A. H. Low, and others.

Action of Potassium Permanganate upon Sodium Hyposulphite.—M. Hönig and E. Zatzek have stated that in alkaline solutions the alkaline hyposulphites are completely converted into sulphates by potassium permanganate even in the cold. M. Gläser has examined the equation of decomposition proposed by the former chemists and pronounced it incorrect. Hönig and Zatzek had further stated that in neutral solutions the oxidation of the hyposulphites by permanganate is incomplete. Gläser, on the contrary, obtained a complete transformation of sodium hyposulphite into sulphate by adding solution of permanganate to the boiling solution of the former salt until a permanent redness was produced. Hönig now replies that his oxidation experiments in neutral solutions were conducted not at a boiling heat but at ordinary temperatures.

The Precipitation of Silver Chloride, Bromide, and Iodide from Solutions containing Antimony Oxide and Tartaric Acid.—R. Schneider.—From *Journal für prakt. Chemie*.

The Alkaloids of the Cinchona Barks.—O. Hesse.—From *Liebig's Annalen*.

The Analysis of Gaseous Haloid Compounds of the Hydrocarbons.—Carl Seubert.—From the *Berichte der Deutsch Chem. Gesellschaft*.

Determination of the Nitrogen of Organic Substances.—A. Houzeau.—Noticed under *Comptes Rendus* (vol. c., p. 1445). It is here stated that the same method was proposed some years ago by C. Arnold. The methods of Ruffe and of Dumas (the latter according to the modification of S. W. Johnson and E. H. Jenkins) have been compared by C. W. Dabney, Jun., and B. von Herff with fairly concordant results. J. Cosack has compared König's oxidation and reduction method with the processes of Varrentrapp, Ruffe, and Grete. With certain guanoses, especially those rich in ammonium urate, it gives lower results than the other methods. C. Brunnemann and F. Seyfert (*Chemiker Zeitung*) give certain directions for the execution of Kjeldahl's method. They recommend round-bottomed boiling flasks supported on wire network. They find that the addition of phosphoric anhydride prevents bumping. R. Warington (*CHEMICAL NEWS*) has examined the applicability of Kjeldahl's process in presence of nitrates.

Determination of Gaseous Cyanogen in Presence of Carbon Dioxide and Monoxide, Nitrogen, and Oxygen.—G. Jacquemin.—Noticed under *Comptes Rendus*.

The Titration of Phenol with Bromine.—Carl Weinreb and S. Bondi.—In carrying out Koppeschaar's method only 6 atoms of bromine are consumed, or appear to be consumed, to 1 mol. phenol. They point out that this method gives good results with pure phenol, but that it is unsuited for the determination of phenol in crude carbolic acid.

Detection of Liquorice in Beer.—R. Kayser.—For this paper the reader is referred to the *Chemiker Zeitung* (ix., p. 781).

Determination of Gluten.—Balland.—From the *Comptes Rendus*.

Detection of Oil of Turpentine in Oil of Citron.—G. Heppe.—The sample is heated to 172° in a dry test-tube with dry pulverised copper butyrate. Pure citron oil dissolves this salt with a green colour. In presence of oil of turpentine the mixture becomes turbid yellow and deposits cuprous oxide.

Examination of Fats and Oils.—A series of passages from *Dingler's Journal*, the *CHEMICAL NEWS*, the *American Chemical Journal*, the *Analyst*, and the *Chemiker Zeitung*.

Composition and Analysis of Wax.—Otto Hehner.—From the *Analyst*.

Determination of Metallic Zinc in Zinc Powder.—Morton Liebschütz.—The author moistens 1 grm. of the sample, after removing any metallic iron by means of a magnet, with alcohol in a beaker glass, stirs it with a small platinum rod, and covers it with a warm neutral solution of 5 grms. copper sulphate. After digesting for some minutes the mixture is acidified with a few drops of dilute sulphuric acid. After the copper has deposited the liquid is poured through a small filter, and the deposit is washed by decantation with warm water until copper can no longer be detected in the filtrate by means of potassium ferrocyanide. The copper along with the ash of the filter is then dissolved in nitric acid, any lead here present is removed, the solution is made up to a known volume, and the copper is determined volumetrically in an aliquot part thereof by means of potassium cyanide. Kosmann (*Chemiker Zeitung*) remarks that he proposed this method in 1883 and described it in full.

Determination of Nitric Acid in Manures.—Shepherd and H. B. Yardley.—From the *CHEMICAL NEWS*.

Testing Commercial Feeding-Stuffs.—A. Emmerling (*Chemiker Zeitung*).—The meals, foods, comminuted cake, &c., are introduced into stoppered bottles which

have previously undergone an elaborate purification and are made up into a thin paste with distilled water. The bottles are then placed in a stove at 35°, and, after twenty four hours, portions are submitted to microscopic examination.

Adulteration of Menthol with Thymol.—F. A. Flückiger.—The author doubts the possibility of this sophistication, as, if these two substances are mixed in equal parts, both become liquefied. Menthol is also mixed with paraffin, the solid fats, and camphor.

Testing Cocaine Hydrochlorate.—H. Beckurts.—A solution of 0.01 of the sample in 25 c.c. of water should not become brown on the addition of a drop of decinormal permanganate, and, on the addition of a few more drops, becomes turbid in consequence of the formation of a violet-red precipitate.

Examination of Quinine.—C. H. Wood and E. L. Barret.—From the *CHEMICAL NEWS*.

Determination of Morphine in Opium.—W. Bernhardt.—The author rubs up 1 grm. powdered opium with water, filters, washes the undissolved matter with water until the washings run off colourless and a drop tested with ferric chloride no longer shows the presence of meconic acid. For this purpose 30 to 40 c.c. of water are necessary. The solution is evaporated down to 25 c.c. and mixed in a test-tube with 5 drops of ammonia and 10 c.c. of ether, shaking frequently. After standing for twelve hours the ether is completely removed by decantation and the application of blotting-paper, the morphine which separates out as a crystalline powder is collected on a tared filter, the last traces of the mother-liquor displaced by a little ether, dried, and weighed.

Examination of Solutions of Morphine.—Egeston, Jannings, and Bedson.—From the *Lancet*.

Applicability of Kjeldahl's Method in Metabolic Researches.—C. Arnold.—The author has obtained satisfactory results.

Determination of Urea with Bromine-Water.—E. Salkowski.—The author uses the apparatus proposed by Schulze-Tiemann for determining nitric acid in water as nitric oxide. The urine is diluted with 5—10 parts of water and 25 c.c. are then placed in the flask, an equal volume of water is added along with 2 drops of hydrochloric acid, the stopper, bearing the tube connections is inserted, the gas-delivery tube is closed, and the flask is heated to an incipient boil. The flame is then withdrawn, the ascending tube filled with hot water, the clamp of the gas delivery tube opened, and the flask boiled free from air. When this has taken place the clamp is closed, a considerable quantity of bromine-liquor (prepared from 5 c.c. bromine, 60 c.c. soda-lye of sp. gr. 1.34, and 30—35 c.c. water (previously well boiled) is allowed to enter, and the liquid heated to a boil after closing the clamp of the ascending tube, until over-pressure is perceptible. If the caoutchouc portion of the delivery tube is then set free the nitrogen streams into the measuring-tube. To obtain it entirely the boiling is continued for some time.

On Neubauer's Determination of Creatinine in Urine.—E. Salkowski.—In this memoir, taken from the *Zeitschrift f. Physiol. Chemie*, the author suggests certain improvements on Neubauer's process, for which we must refer to the original.

On Heteroxanthine.—G. Salomon.—Heteroxanthine occurs in the mother-liquors from the preparation of paraxanthine, from which it readily separates, owing to its sparing solubility.

Detection of Biliary Colours in Urine.—C. Deubner.—The author gives the preference to the reactions of Rosenbach and Hilger.

Separate Determination of Albumen and Globulin.—Neutral ammonium sulphate completely precipitates the true albumens from their solutions, the globulin being first precipitated and then the albumen.

Detection of Oxalic Acid in Urine.—E. Salkowski.—An application of Neubauer's process of determining creatinine. The alcoholic precipitate contains, along with chlorides, calcium sulphate and urates, and calcium oxalate. By repeated washing with alcohol at 80 per cent and a little hot water, solution in a little dilute hydrochloric acid, neutralising with ammonia, acidulation with acetic acid, and standing for 24 hours, calcium oxalate is separated out in well-developed crystals.

Determination of Phosphoric Acid in Presence of Iron and Aluminium.—Julius Laubheimer (*Chemiker Zeitung*).—The solution (25 or 50 c.c., containing 0.1 = 0.2 gm. phosphoric acid) is mixed with 10 c.c. solution of citric acid (500 grms. per litre), and then with a large excess of strong ammonia. After the mixture has become somewhat cool it is precipitated with 15 to 20 c.c. of the ordinary (not sulphated) magnesia mixture. The crystalline ammonium-magnesium phosphate is filtered off after standing 12 hours and is washed first with ammoniacal water and then with alcohol. By ignition over the ordinary burner there is obtained white magnesium pyrophosphate, which rarely requires to be moistened with nitric acid. In strongly ferriferous phosphates (*e.g.*, Thomas and Gilchrist slags), 20 c.c. of citric acid are used and a corresponding increase of ammonia. It is then necessary, after adding the magnesia mixture, to stir the liquid for some minutes until it has become turbid.

Application of the Marsh-Berzelius Method to the Quantitative Determination of Arsenic.—W. P. Headden and B. Sadler.—It is merely mentioned that the results have not been encouraging.

The Ptomaines.—The results of the Italian Commission are given in a book of 75 pp.

Reaction for the Identity of the Strychnos Preparations.—O. Schweissinger.—A granule of the extract, if heated in a porcelain capsule with a drop of dilute sulphuric acid, gives an intense violet colour, which disappears on dilution with water and re-appears on concentration. This reaction is due, no. to the alkaloids, but probably to the glucoside loganine.

Observations on Poisoning by Atropine.—J. Kratzer.—A perfect demonstration of the presence of atropine can be reached only by means of physiological experiments.

Unity of Atomic Weights.—L. Meyer and K. Seubert.—The authors point out as a source of confusion that the atomic weight of oxygen is in some cases assumed = 16 and in others = 15.96. They recommend that the former value should be set aside.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Note on Prussian Blue as a Colouring-Matter of Sandstone.—I noticed in a wall near where I live three or four pieces of sandstone of a blue colour, and thinking this rather peculiar I took a piece of it for examination. The sandstone is of a yellowish brown colour, with here and there streaks and masses of a blue colour. Judging from appearances I should have said the colour was due to copper, but upon testing for copper I could not find any. Iron was found to be present both in the colouring matter and in the rock itself; a ferrocyanide was also found to be present, and this of course conclusively proved that the colour was due to Prussian blue (ferric ferrocyanide). It might be thought that the colour is not natural, but as the colour has penetrated right into the centre of the stone we cannot doubt but that it has been formed in a natural manner; how it has been formed I cannot say, but it is evidently by the action of some substance on the ferric hydrate contained in the rock.—H. B. S.

ERRATA.—P. 71, col. 2, line 6 from bottom, for "telegraphene" read "telegrapheme." Line 8 from bottom, italicise "cle." Line 13 from bottom, for "substantially" read "substantivally."

TO CORRESPONDENTS.

W. P.—See review of "Art of Soap-Making," in CHEM. NEWS, vol. lli., p. 199.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1395.

ON THE PREPARATION OF IODALDEHYD.

REMARKS ON THE PAPER OF MESSRS. W. POPPLEWELL
BLOXAM AND E. F. HERROUN.

By P. CHAUTARD.

IN the CHEMICAL NEWS of 25th June last (vol. liii., p. 301) there is an interesting article by Messrs. Popplewell Bloxam and Herroun, on Iodaldehyd, in which these gentlemen make some observations on a memoir which I presented on this subject to the Academie des Sciences at the commencement of the year, and which has been printed in the *Comptes Rendus*. In reply to these observations and to some questions I have prepared the accompanying note, which I shall be very pleased to see printed in your estimable journal.

It is now some time since Aimé and Johnston, in order to order to obtain an iodised derivative of aldehyd, oxidised an alcoholic solution of iodine by means of nitric acid, but they only gave very little attention to this reaction, and their results were not very reliable; they evidently only obtained mixtures.

Messrs. Popplewell Bloxam and Herroun have made fresh researches on this oxidation, and the results of their work form an interesting memoir which appeared in this paper (CHEMICAL NEWS, vol. liii., p. 301). Besides nitric ethers and cyanogen derivatives, they have obtained a body whose properties resemble very closely those which I have already described as belonging to iodaldehyd. Although they have not been able to isolate it, nor for that reason to analyse it, I feel certain that the product they have been dealing with is identical with that which I prepared myself by the action of a mixture of iodine and iodic acid on an aqueous solution of aldehyd. Their product decomposes when distilled at a temperature of 80°: this is the same point of decomposition that I found. Its smell and irritating action on the mucous membrane, its easy transformation into iodoform under the influence of bases, belong also to iodaldehyd, and, further, the manner in which it behaves with the different reagents show a still greater similarity.

I regret that these gentlemen did not try the effect of bisulphite of soda, ammonia, and cyanide of potassium; they would, in all probability, have obtained the combinations which I prepared and described, and which would have proved beyond all doubt the identity of the two bodies.

Messrs. Popplewell Bloxam and Herroun have tried to prepare iodaldehyd by my process; they have followed to the letter the instructions I gave, and, although they say they have had proof of its presence, they have not been able to isolate it. I have been searching for the reason of this non-success.

In my memoir to the Academie des Sciences I recommended using 50 grms. of aldehyd at a time; this quantity appeared to be too much to Messrs. Popplewell Bloxam and Herroun, who used very small quantities. I have been thinking that the mass of the product and the duration of the operation might have an influence on its success: to verify this I made a preparation of iodaldehyd, starting with 5 grms. only of aldehyd, and I succeeded perfectly. Thus, when one proceeds in the manner I have indicated, the question of quantity has no influence on the results.

As far as the duration of the operation is concerned, I have already published the fact that the reaction is com-

pleted in three or four days in the summer and eight days in the coldest part of winter. Now Messrs. Popplewell Bloxam and Herroun have remarked that in all their experiments the duration of the operation has been much longer than I have indicated, and sometimes as long as several weeks. This is entirely a question of temperature. In the course of my experiments the matrass in which I carried out the operations remained in the laboratory on a staging placed over a stove, and where the temperature averaged 30° to 40°. In the case of these gentlemen the temperature was doubtless lower, and that explains the abnormal duration of the operation. In my opinion it is entirely because their operations have been conducted too slowly that Messrs. Popplewell Bloxam and Herroun have not been able to precipitate an appreciable quantity of iodaldehyd by the addition of water. In fact I have several times had to leave a matrass, in which I have prepared iodaldehyd, for several weeks after the action was completed, and when, after this lapse of time, I added water to precipitate the iodaldehyd, I noticed that the quantity of heavy oil which fell was always notably less than the quantity I should have had (one-fourth to one-fifth less than the normal yield), and further, that it was charged with a large quantity of iodine. This is owing to the fact that iodaldehyd is partially decomposed after long contact with water.

In the case of Messrs. Popplewell Bloxam and Herroun the reaction proceeded very slowly; at the moment when the solution of the iodine was complete a part of the iodaldehyd produced was already decomposed, by cause of its prolonged contact with the water, and when they added more water the iodaldehyd which still remained was not present in sufficient quantity to supersaturate the water, and thus to become precipitated; it dissolved entirely, and its presence in the liquid was only noticed by the manifestation of properties which these gentlemen have observed, and which agree with the description which I gave of the properties of iodaldehyd.

At the commencement of my researches I operated on small quantities of matter and at low temperatures,—that is to say, under conditions analogous to those in which Messrs. Popplewell Bloxam and Herroun have been working, and I had much trouble in getting any results; it is only by using large quantities that I have been able to succeed in my work.

The purity of the iodic acid used is also of some importance; it occasionally happens that the iodic acid, especially when it is well crystallised, retains considerable quantities of sulphuric acid; in this case the sulphuric acid is set free by the solution of the iodic acid, and it decomposes a part of the iodaldehyd as it gradually forms: this is another cause of failure.

I did not specify all the conditions for successful working in my note to the Academy of Sciences, because my note there was only preliminary, and sent in principally to take precedence, and to reserve to myself the continuation of this research; besides this, I have since introduced modifications into my mode of working, which I shall publish before long. I have also succeeded in preparing iodaldehyd by different methods, notably by the action of iodine on the aldehydate of ammonia. Further, I have applied the same process of ioduration to a certain number of aldehyds of the fatty series, and I have obtained a whole series of combinations which I shall make known in a paper towards the end of the year.

To sum up, I keep to the terms of my memoir, that in operating exactly as I have described we can produce iodaldehyd with the greatest ease. I do not mean, be it well understood, anything beyond common iodaldehyd, for the purification of this body is an excessively long and difficult operation; it is necessary to start with 500 grms., at least, of impure iodaldehyd, to obtain 15 or 20 grms. in the state sufficiently pure for analysis.

Messrs. Popplewell Bloxam and Herroun, in the course of their paper, quote a work of Schoonbroodt on iodal. The conclusions of this author are erroneous. He pre-

tends to have obtained, by the action of an aqueous solution of hypochlorite of potash, or an alcoholic solution of iodine, a crystalline precipitate, which resolved itself into iodoform and formic acid under the influence of bases, and which he named iodal. I have often repeated this experiment, and I am convinced that the crystalline precipitate which does in fact form is composed exclusively of iodide of potassium and iodoform; this latter is produced by the action of the free potash which always occurs in solutions of hypochlorite of potash, or the alcoholic solution of iodine. I have never noticed, no matter how carefully I have worked, the presence of any other body whatever.

Messrs. Popplewell Bloxam and Herroun have done me the honour of asking me to explain the reaction in virtue of which iodaldehyd is transformed into iodoform. It is impossible for me to answer them on this point, but I have undertaken a research with the idea of elucidating this question, and I hope before long to arrive at a satisfactory result.

47, Rue Olivier de Serres, Paris,
August 9, 1886.

BEHAVIOUR OF MAGNESIA CONTAINING RARE EARTHS (?).

BY GEORGE STILLINGFLEET JOHNSON.

SOME *calcined magnesia* (Hopkin and Williams) was allowed to slake under cold water, when the reaction of the water was found to be strongly alkaline. This alkalinity being attributed to sodium carbonate, the hydrated magnesia was subjected to prolonged washing by decantation with boiled distilled water. It was observed that, although the water above the precipitate had always a very marked alkaline reaction immediately after *thorough stirring*, this reaction disappeared after standing some hours at rest, though no turbidity appeared in the supernatant liquor. The washings gave a crystalline precipitate with ammonia and ammonium oxalate on prolonged standing. At this stage—the washing having been continued for many days, and the presence of alkali metals being considered extremely improbable—some of the precipitate was dissolved in HCl, and the solution poured upon the remainder together with about 2 litres of distilled water. The precipitate was then frequently stirred with the supernatant solution, heat being also applied from time to time. Still the same alkaline reaction was apparent immediately after stirring, and disappeared on standing.

After about a week's digestion the supernatant liquor was decanted off and precipitated by baryta water. The filtrate was freed from Ba by ammonium carbonate, and the filtrate from BaCO₃ was evaporated to dryness, and ignited to expel ammonium salts. The residue, after ignition, was extracted with water, and the portion insoluble in water was dissolved in HCl.

The aqueous solution gave precipitate with H₂SO₄, also with Na₂HPO₄ in alkaline solution. No precipitate with (NH₄)₂CO₃, even on boiling.

The acid solution gave very little precipitate with dilute H₂SO₄, but a very abundant precipitate with Na₂HPO₄ in alkaline solution. No precipitate with (NH₄)₂CO₃, even on boiling.

The MgO is therefore supposed to contain an earth whose oxide is soluble in water and very alkaline, whose carbonate is soluble, whose sulphate is insoluble; also another earth whose sulphate is soluble, but its phosphate insoluble in alkaline solution, its carbonate being also soluble, like the first.

King's College Laboratory, August, 1886.

Distinction between the Milk of Women and of Cows.—E. Pfeiffer and J. Schmidt.—The casein of the former milk, like the latter, is precipitated by acids if heated, but the former falls in fine flocks.—*Zeitschrift*,

REDUCTION OF CARBON DIOXIDE BY POTASSIUM CYANIDE.

By ARNOLD EILOART, B.Sc.

POTASSIUM cyanide placed in a porcelain boat and heated in a combustion-tube traversed by a stream of CO₂ dried by H₂SO₄, blackened; fused; whitened again; increased in weight; and caused formation of carbon monoxide. Later, as the heat was increased till the glass was near fusing, the substance began to volatilise, losing weight; when, after many days, the formation of gas unabsorbed by potash ceased, the weight was but a third of the original. The residue was practically all potassium cyanate, of which the cyanide used had contained a mere trace. The amount of KCy oxidised is calculated on the percentage (97·8) which the substance contained when put into the tube; but it was observed that always after weighing the white residue it darkened at first on heating, so that a minute portion was probably decomposed owing to momentary exposure to moist air in transferring the boat to the stoppered tube in which it was weighed; for pure KCy is said not to blacken on heating, and this specimen (once the blackening first formed had burnt off) did not darken when cooled and re-heated without opening the tube.

Substance taken—0·131 grm., containing 97·8% or 0·126 grm. KCy. CO found—42·7 c.c. at zero and 760 m.m. = 0·0538 grm. Theory—0·0543 grm. for the equation

$$\text{KCy} + \text{CO}_2 = \text{KCyO} + \text{CO}.$$

King's College Laboratory, August, 1886.

VERIFICATION OF THE CALCULATION OF THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 79.)

X. Relation between Silver and Potassic Chloride, γ 14—26.

IN the year 1860 (a 271, 272) M. Stas had already published twenty-one estimations of this relationship, in which he put almost absolute confidence (a 256, 332). In 1857, however, G. J. Mulder† showed that the solution of nitrate of silver, with a chloride carefully added until the solution was clear, still gave a precipitate with a decinormal solution of nitrate of silver. By adding this solution very cautiously we reach the *silver limit*, where the liquid is no longer troubled by nitrate of silver, but is by a chloride. To get from one limit to another, which can be repeated indefinitely, it is necessary to have quantities of silver and chloride exactly equivalent. Mulder concludes that the mean of these limits represents the true proportional relationship. In this manner the liquid shows an opalescence of equal intensity with the same volumes of decinormal solutions of salt and nitrate of silver. The same reaction occurs in the case of nitrate of silver and hydrochloric acid. When M. Stas published his first two memoirs he did not ignore this *reciprocal precipitation*, which, by-the-bye, had been observed previously by Mulder, Gay-Lussac, and the chemists of the Hotel de la Monnaie at Utrecht. M. Stas‡ communicated some minute researches on this subject in 1872 and 1874. He noticed that chloride of silver, *broken up* or *powdered*, is *soluble in water*, to the extent of 13 m.grms. per litre, and that it is eliminated from its solution by the addition of a quantity of chlorine or silver *three times* as much as that which dissolved in the state of combination.

All the estimations of silver, its chlorides and bromides

* *Ann. Chim. Phys.*, 6th Series, vol. vii., April, 1886.

† "De Essaycermethode van het Zilver," Rotterdam, 1857.

‡ *Annales de Chimie et de Physique*, vol. xxv., p. 22, 1872, and vol. iii., pp. 145 and 289, 1874.

have been done according to the method that Pelouze suggested to Marignac in 1842. The salt and the silver are weighed as accurately as possible, and their solutions are then mixed. Then the slight residue of silver or of the halogen which remains uncombined is weighed.

In the estimations published in 1860 and 1865 M. Stas always added the salt solution until the cessation of all precipitates (α 269, β 47). Thus it was the limit of salinity that he determined. After his researches on the solubility of chloride of silver he considered it to be a duty to submit his previous work to a severe control, by determining (first method) the saline limits of silver, of which the arithmetic mean would be the true relationship, and (second method) the point when the opalescence of the liquid is the same as that produced with decimal solutions.*

I cannot understand why the relation found in 1860 or 1865 should always be *lower* than that of 1882, nor why the difference reaches $\frac{1}{10000}$ for chloride of potassium and is hardly anything for chlorides of sodium and ammonium. Whatever may be the reasons, the estimations of 1882 are the most exact, and are the only ones which I have used in my calculations.

For chloride of lithium we must be contented with the experiments of 1865, because M. Stas has not repeated them.

Bromide of silver is altogether insoluble in cold water, and does not show the complications described in the above determinations. It is for this reason that M. Stas prefers bromine to chlorine for the silver determinations.

To obtain equal weights of silver and of halogen salts I subtracted from the weight of silver used the weight of the superfluous metal, or added the weight of silver which was wanting to the supernatant liquid of the chloride or bromide of silver first formed.

After these necessary explanations I give the tables of results, adding the quantity of silica contained in the halogen salts.

(To be continued.)

THE SEPARATION OF ANTIMONY AND TIN.

By AD. CARNOT.

THE author has sought to apply to this problem a method analogous to that which has proved successful for the separation of zinc and cadmium, founded on the simultaneous use of oxalic acid and sodium hyposulphite. Oxalic acid in faintly acid hydrochloric solutions of tin and antimony gives white crystalline precipitates of the simple oxalates of these metals. In presence of an ammoniacal salt there are formed double oxalates much more soluble than the foregoing. These salts crystallise only from crystalline solutions, and they may be diluted with much water without turbidity. They consequently can yield solutions of tin and antimony very faintly acid and yet perfectly limpid, conditions favourable for the analyses. These solutions of oxalates have some analogy with those of the double tartrates. One of the simplest methods of preparing them consists in pouring into the solution of the metallic chlorides, according as it is more or less acid, ammonia or ammonium chloride, then oxalic acid, and lastly ammonia to almost complete saturation. If a precipitate forms it is re-dissolved by a trifling excess of oxalic acid. In such a solution sulphuretted hydrogen precipitates entirely the antimony as an orange sulphide; with stannous salts it gives a black precipitate; it precipitates the stannic salts incompletely, especially if the solution is hot and contains a rather large proportion of

free oxalic acid. The black colour of the stannous sulphide attracted the author's attention. Such, he finds, is the true colour of stannous sulphide when absolutely pure; the maroon-brown ascribed to it in the text-books is due to a mixture of the black stannous sulphide with a larger or smaller proportion of the yellow stannic sulphide. If we pass a current of hydrogen sulphide into a hydrochloric solution of stannous oxide, there is produced a brown precipitate; in the oxalic solution of the same salt the precipitate is at first of a fine black, but if it is allowed to cool in a stoppered bottle the black deposit of stannous sulphide soon becomes covered with a thin yellowish layer of stannic sulphide.

Sodium hyposulphite in a hydrochloric solution of tin, at a boiling-heat, produces a yellowish white precipitate, containing sulphur and tin sulphide and oxide. In an oxalic solution, on the contrary, only sulphur is deposited, all the tin remaining dissolved. Sulphurous and sulphuric acid no longer produce in it any precipitate, contrary to what happens in a faintly acid hydrochloric solution.

As for the antimony salts, acidified either with hydrochloric or oxalic acid, they yield, on boiling with hyposulphite, an escape of sulphurous acid, and a precipitate, yellow at first, but passing into orange, vermilion, and then to cinnabar-red. This precipitate consists of sulphur and antimony oxysulphide. If it is carefully washed and dried, heated to about 110° , and, if the free sulphur is dissolved out with carbon disulphide, the residue—which is of a fine red—answers exactly to the formula Sb_2OS_2 .

The precipitation is complete only at a boiling-heat, and in presence of a small quantity of free hydrochloric acid. It is in danger of remaining imperfect if the liquid is acidified only with oxalic acid.

As a consequence of the foregoing observations, and after very numerous experiments, the author advises the following procedure for the rapid and exact separation of the two metals:—

The hydrochloric solution of tin and antimony is mixed with ammonia or ammonium chloride; about 2 grms. of oxalic acid, previously dissolved, are added and then ammonia almost to saturation. The liquid is diluted to 250 or 300 c.c., and there is added a solution of hyposulphite containing at least 10 parts of this crystalline salt to 1 part of the antimony to be determined. The liquid, which is clear at first, becomes turbid on heating and passes successively to yellow and red. From 1 to 22 c.c. of dilute hydrochloric acid are added and the boiling is kept up for some minutes. On ceasing to heat the red precipitate is deposited and the liquid quickly becomes clear. On adding, further, a few drops of hydrochloric acid and boiling for some moments, we observe the aspect of the liquid. If it remains clear a little hyposulphite must be added. If it is milky and entirely white the precipitation of the metal is complete. But if it takes a yellow or reddish colouration, antimony remains in solution, and the addition of acid (and sometimes of hyposulphite also) must be repeated until the turbidity is purely white. The oxysulphide, mixed with sulphur, is collected on a tared filter, where its consistence allows it to be easily washed. If a red coating of oxysulphide adheres to the glass, it is taken up with a minimum of hydrochloric acid, the hydrogen sulphide is expelled, the liquid is diluted and again precipitated with hyposulphite at a boil; or it may be dissolved with 3 or 4 drops of hydrosulphate (ammonia), and after dilution it is decomposed with hydrochloric acid. In either case the precipitate is added to the former upon the filter. The filtrate contains all the tin; it is saturated with ammonia while still hot; the precipitate is re-dissolved in hydrosulphate and the sulpho-salt is decomposed with acetic acid. Hydrochloric acid is not applicable. In a short time the precipitate subsides and is received on a filter, washed with water and a little ammonium nitrate, dried, and ignited in a porcelain crucible, and weighed as stannic oxide. As for the antimony oxysulphide, it is always mixed with an

* Mulder discovered the first method, while the second has been used since 1839 in the Monnaie d'Utrecht, where it was introduced by Van Setten. It was also Van Setten who discovered the solubility of chloride of silver in pure water.—*Journ. de la Soc. Hollandaise de Pharmacie* (Tydschrift van Haaxman, 1858, p. 15).

excess of sulphur, and may be converted into antimony tersulphide by simple calcination in a current of dry carbonic dioxide. Or, after having separated the two metals as above, the red oxysulphide may be dissolved in hydrochloric acid whilst still moist, and the antimony may be determined volumetrically.—*Comptes Rendus*, ciii., p. 258.

ON THE CHEMICAL COMPOSITION OF HERDERITE AND BERYL,

WITH NOTE ON THE PRECIPITATION OF ALUMINUM AND
SEPARATION OF BERYLLIUM AND ALUMINUM.*

By S. L. PENFIELD and D. N. HARPER.

I. Composition of Herderite.

THE rare material for carrying on the present investigation of herderite was given to us by Mr. L. Stadtmüller and Prof. George J. Brush. The crystals were carefully picked by hand, and freed as far as possible from all foreign matter. They were then crushed and sifted, and suspended in the Thoulet solution; only the material whose specific gravity was greater than 2.95 was used for analysis. By this means there was separated from the hand-picked crystals a little questionable material, which was used in making a sort of preliminary analysis, and we were able to obtain over 5 grms. of very pure material. Before making the separation with the Thoulet solution we carefully took the specific gravity of some of the purest crystals by taking the specific gravity of the solution in which they were suspended without floating or sinking. This we found to be from 3.012 to 3.006, the heaviest being the specific gravity of a very clear transparent crystal, while the more opaque and cracked crystals were a trifle lighter. The mineral is so much heavier than the quartz and felspar to which the crystals were attached that we feel very confident of the purity of the material which we analysed.

The analysis was made after we had had considerable experience in the determination of beryllium, and had made some experiments in determining it in presence of phosphoric acid. The method which we adopted gave good satisfaction, and we give it here somewhat in detail. The mineral was dissolved in nitric acid, the solution concentrated to a small volume, sulphuric acid was added, and the gypsum crystals—after being collected by filtering through a rubber funnel—were ignited and weighed as CaSO_4 . The filtrate was concentrated in a platinum dish, and gently ignited to drive off all hydrofluoric acid and the excess of sulphuric acid. The residue was dissolved in hydrochloric acid, a basic acetate precipitation of a part of the beryllium and phosphoric acid was made in the cold with ammonium acetate, and a little calcium precipitated from the acetic acid filtrate by ammonium oxalate, which was ignited and weighed as CaO . The beryllium in the filtrate from calcium oxalate was precipitated as a phosphate by means of ammonia, filtered, and the phosphoric acid in the filtrate precipitated with magnesia mixture. The two precipitates containing the beryllium as phosphate (the basic acetate precipitate contained the bulk of the beryllium) were ignited in the same crucible and fused with sodium carbonate. The fused material was soaked out in water, phosphoric acid obtained in the solution by the usual method, while the insoluble beryllium oxide was dissolved in hydrochloric acid, precipitated with ammonia, weighed, and the trace of P_2O_5 contained in it separated with ammonium molybdate. The P_2O_5 and bases in analysis III., on which we place the greatest confidence, were separated and determined in the above manner.

Other determinations are given to show the accuracy of the method. The CaO in II. was all obtained in the

filtrate from the basic acetate precipitation, and was not partially precipitated as gypsum. The BeO in the same analysis was tested for Al_2O_3 , but not more than a questionable trace could be detected. The P_2O_5 in I. was from a direct determination with ammonium molybdate, but a very slight mechanical loss was incurred. The fluorine was determined in III. by driving off the silicon fluoride and titrating the hydrofluosilicic acid by means of a standard alkali.* After making the determinations fresh U-tubes were connected with the apparatus and the aspiration carried on for several hours, but no more silicon fluoride was driven off. As our alkali had just been standardised by means of sodium carbonate and test experiments on fluor-spar, we feel very confident that the fluorine determination is correct. The water determinations are somewhat surprising. Mackintosh† made no tests for water, and considered the mineral to be an anhydrous phosphate with fluorine. Winkler‡ made no determination of fluorine, and obtained no satisfactory tests for that element by etching glass. He obtained a loss by ignition, however, of 6.59 per cent in the Stoneham mineral by strong ignition, which he regards as water. Genth§ obtained 6.04 per cent of fluorine by direct determination, and 0.61 per cent of water by heating the mineral with lead oxide to bright redness. Mackintosh|| obtained good tests for fluorine by etching, and found a loss of 6.03 per cent by strong ignition. He proved conclusively that fluorine was given off by strong ignition, and concludes that it is replaced, in part at least, by oxygen. We are scarcely willing to believe that such a reaction would take place on heating an anhydrous phosphate containing fluorine. Our first water determination was made by weighing out the mineral in a boat, placing it in a combustion-tube containing a layer of dry sodium carbonate, igniting the tube to full redness, and collecting the water in a weighed chloride of calcium tube. We obtained 0.69 per cent; afterward the mineral was dissolved, and analysis II. completed from the same material. After almost completing our analysis, and finding only 5.27 per cent of fluorine, we tried the following experiments. A little herderite powder was placed in a hard glass tube, sealed at one end, and ignited. At first only a slight film of water condensed in the cold part of the tube; by strong ignition over the blast lamp, however, there was a sudden evolution of hydrofluoric acid, which etched the glass very perceptibly near the mineral and deposited a film of silica and very acid water, as marked as in an ordinary reaction for fluorine in a closed tube with acid sulphate of potash. In our experience we have never seen any hydrous fluoride which gives off such strongly acid water and such a marked fluorine reaction. Some of the powdered mineral was placed in a closed glass tube, covered with a layer of dry sodium carbonate, and strongly ignited; neutral water was given off and condensed as a ring, which indicated more than a trace of water. The water was obtained in the following way:—About 2 grms. of calcite were ignited over the blast lamp till a constant weight was obtained. The mineral was then weighed into the same crucible, the lime was slaked with water, the contents of the crucible were carefully dried and then ignited till constant weight was obtained, the water being calculated from the loss of weight. The slaking of the lime makes an intimate mixture of the mineral with the lime, and a preliminary experiment proved to us that only neutral water was driven off. In I. there was a slight mechanical loss in slaking the lime, which caused the water determination to be too high, the P_2O_5 too low. In III. the water was obtained from a larger quantity of mineral. No sublimate was formed on the cover of the crucible by the volatilisation of any fluoride. The analyses were made on air-dry powder

* *Amer. Chem. Journal*, i., 27.

† *Amer. Journ. of Science*, III., xxvii., 135.

‡ *Neues Jahrbuch für Mineralogie*, 1884, ii., 134.

§ *Proc. Amer. Phil. Society*, xxi., 1884, 694.

|| *Amer. Journ. of Science*, III., xxviii., 401.

* From the *American Journal of Science*, vol. xxxii., p. 107.

which lost 0.10 per cent by drying for one hour at 100° C. The beryllium precipitates were always of a light cream-colour after ignition, indicating that not more than a minute trace of iron was present.

The following quantities of mineral were used in making the analyses:—I. 0.4552 grm.; II. 1.0029; III. P_2O_5 and bases 0.7336, F 0.9692, H_2O 1.1612.

	I.	II.	III.	Ratio.		Calculated.
P_2O_5	43.47	—	43.74	0.308	1.00	43.83
BeO	—	15.28	15.51	0.620	2.01	15.44
CaO	—	33.61	33.67	0.601	1.95	34.57
F	—	—	5.27 ÷ 38	0.138	0.343	5.86
H_2O	4.37?	—	3.70	0.205		2.77
			101.89			102.47
O equivalent of F..			2.22			2.47
			99.67			100.00

The ratio of $P_2O_5 : BeO : CaO : (F_2 + H_2O) = 1 : 2 : 2 : 1$ nearly. The high temperature at which the water is driven off indicates that it is not water of crystallisation, but is very firmly united in the mineral as hydroxyl, every H_2O representing two hydroxyl groups, and the OH being probably isomorphous with F. The ratio of F:OH is nearly 1:1, or more nearly 3:4 in our analysis. In the calculated analysis we have used the ratio F:OH = 1:1, but recognise that it is probably simply a case of isomorphism. The composition of herderite is, therefore, an isomorphous mixture of $CaBeFPO_4$, with $CaBe(OH)PO_4$, which may be written $CaBe(FOH)PO_4$, or a salt of phosphoric acid, two of whose hydrogen atoms have been replaced by a bivalent element, and the third likewise by a bivalent element whose other free affinity has been satisfied by a fluorine atom or hydroxyl. This is the same composition as that proposed by Mackintosh, except that he regarded the mineral as simply the fluorine compound, and did not detect the water. Chemically herderite is closely related to the three minerals—wagnerite, triplite, and triploidite—whose compositions are respectively Mg_2FPO_4 , $(FeMn)_2FPO_4$, and $(FeMn)_2(OH)PO_4$. These three minerals offer the best illustration we have of the isomorphism of F and OH, and we feel that we have in herderite another strong proof of the correctness of this interesting relation. In crystallisation the minerals vary, herderite being orthorhombic, triplite questionable, and wagnerite and triploidite monoclinic. The latter two have, like herderite, a prismatic angle of nearly 120°.

2. Analysis of Beryl.

In 1884 one of us* published a series of analyses which showed that alkalis are present in beryl sometimes to quite a large extent, and that water is always given off by ignition. At the time the analyses were made the author had had little experience in the determination and separation of beryllium, and used the ammonium carbonate method, which seemed to him to be the most accurate. Our experience has taught us that the method used in the manner described in the above-mentioned article gives too low results for beryllium, and the analyses are only of value as showing to what extent alkalis and water are present in beryl. Since the publication of the article it has always been the author's wish to make a series of experiments on the separation of aluminum and beryllium, and renew the investigation.

We have considered it best not to make a long series of beryl analyses, but to select some very pure beryl and make an analysis of it as carefully as possible. The analysis was made according to the method described at the end of this article, and we feel assured from our experience that the results of the analysis represent the composition of the mineral very closely. The beryl which we selected for analysis was a very pure transparent aquamarine from

Stoneham, Maine, furnished to us by Mr. George F. Kunz, of New York. The mineral was crushed and ground in a steel mortar, and the fine powder boiled in dilute hydrochloric acid, washed, and dried at 100° C. Duplicate analyses were made by both of us, so that we might obtain a very fair average.

Specific gravity, taken on a chemical balance, 2.706.

			Ratio.	
SiO_2	..	65.54	1.092	6.00
Al_2O_3	..	17.75	0.172	0.173
Fe_2O_3	..	0.21	0.001	
FeO	..	0.38	0.005	0.558
BeO	..	13.73	0.541	
CaO	..	0.06	0.001	
Na_2O	..	0.71	0.011	
Li_2O	..	trace		0.61
H_2O	..	2.01	0.112	
		100.39		

The ratio of $SiO_2 : Al_2O_3 : RO : H_2O = 6 : 1 : 3 : 5$ nearly. The ratio of the first three is in the proportion required by the usually accepted formula for beryl. This conclusion was also arrived at by Baker* in a recent analysis made according to the same method which we used. As regards the alkalis, we have as yet no proof that they replace the beryllium, but that is probably the case. Analyses of beryls very rich in alkalis would best settle this question. The water is very constant, about 2 per cent, in all beryls which have come to our notice, with one exception,—Aduntschilon, Siberia,†—and must be in some way very firmly united in the molecule, as it is only given off by very strong ignition. As can be seen by our ratio, there is about one-half a molecule present. Beryls which show a higher percentage of water may, and in some cases which have come under our observation do, contain mechanical inclusions of water. Regarding the water as essential, we would have to add $\frac{1}{2}H_2O$ to the ordinary accepted formula of beryl, or write it $H_2Be_6Al_4Si_{12}O_{37}$. The theoretical composition according to the above formula is—

SiO_2	..	65.81
Al_2O_3	..	18.83
BeO	..	13.71
H_2O	..	1.65
		100.00

We can add also the alkali determinations in the following European beryls. The alkalis were determined by Smith's fusion method and calculated as sodium, although they all contained some lithia. Limoges, France, 0.73 per cent; Hühnerkobel near Bodenmais, Bavaria, 1.20 per cent; Habachthol, Tyrol, 2.26 per cent.

3. On the Precipitation and Washing of Aluminum.

Before making the above investigations we tried a few experiments in the precipitation and handling of aluminum precipitates, which may be of interest to some of our readers. A standard solution of aluminum chloride was first made, containing 0.1002 grm. Al_2O_3 and 1 c.c. pure concentrated HCl in every 50 c.c. which were used in our experiments. The precipitation of the alumina was in all cases made in a volume of about 300 c.c., by neutralising the solution with ammonia till the odour of ammonia could be distinctly obtained from the hot solution; the beaker was then placed upon a lamp-stand and the solution brought to boiling, which was not continued more than one minute. The precipitates were in all cases washed without a pump, but suction-tubes 7 inches long were attached to the funnels, which cause a gentle suction, and if the filter-papers are carefully fitted to the funnels very materially hasten the filtration.

* Amer. Chem. Journ., vii., 175.

† Amer. Journ. of Science, III., xxviii., 29.

* S. L. Penfield. Amer. Journ. of Science, III., xxviii., 25.

The following facts were observed: that precipitates which were made in solutions containing large quantities of acid, either hydrochloric or nitric, filtered as well or better than those from solutions containing little ammonia salts, but on washing with boiling water the precipitates from solutions containing large quantities of ammonia salts became very sticky, washed slowly, so that it was almost impossible to free them from the last traces of ammonium chloride; and that very perceptible quantities of alumina settled out from the filtrates and washings on adding a few drops of ammonia and allowing the beaker to stand in a warm place. Further, that all of the alumina which ran through did so during the washing. The precipitates after they had become slimy and sticky seemed either to be quite soluble in the hot water or else got into such a condition that they readily passed through the pores of the paper and stopped them up, thus hindering the filtration. To make a successful precipitation and washing of alumina it is quite essential not to have very much ammonia salts present, and even with the greatest care it is found that if the filtrates and washings are set away in a warm place, slight precipitates will almost invariably settle out. The above holds good for solutions containing ammonium chloride and nitrate. The fact that alumina passed through the filter only during the washing suggested to us that if we could wash the precipitate with a saline solution which would be completely volatile and do no harm to the precipitate we might avoid the passage of the alumina through the filter and it might also hinder the packing of the precipitate. Ammonium nitrate suggested itself to us as a salt which would be volatile on ignition and do no harm, and our experiments with it have been very satisfactory. The following strength of NH_4NO_3 has been used in all of our experiments—2 c.c. of pure concentrated HNO_3 neutralised with ammonia and diluted to 100 c.c. with water; this strength has proved so satisfactory that we have tried no other. Using this hot saline wash instead of hot water the precipitation can be made in solutions containing large or small quantities of ammonium salts, and no very great care is needed in adding the ammonia. According to our experience, the precipitates from solutions containing a goodly quantity of ammonia salts, resulting we will say from 4 to 8 c.c. of pure concentrated hydrochloric or nitric acid, filter and wash better than precipitates from solutions containing less saline matter. After having made a large number of precipitations we can say that only in one or two cases have we found a trace of alumina in either the filtrate or washings, and that unless the precipitate becomes too dry and packs too firmly upon the sides of the funnel, the washing goes on as well at the end as at the beginning, and there is no difficulty in washing the precipitate free from all traces of chlorine.

Where large quantities of sodium or other fixed salts are to be removed and a second precipitation of the alumina is required, we recommend that the first precipitate after washing be dissolved in nitric instead of hydrochloric acid, then very little washing is enough to free the second precipitate from the last traces of chlorine and fixed salts.

Why ammonium nitrate acts in this way we are not able to state. It may be something on the same principle that sediment deposits much faster in saline than in fresh water. We are convinced that any one who has to handle troublesome alumina precipitates will find the above method of washing of great advantage.

(To be continued.)

On the Combinations of Chloral and Resorcine.—H. Causse.—In the action of chloral upon resorcine there are formed two series of products; the one crystalline, derived from a molecular combination, and the other amorphous, representing a combination of a polymer of chloral with a polymer of resorcine.—*Comptes Rendus*, vol. ciii., No. 5.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To COLONEL SIR FRANCIS BOLTON, *Water Examiner*,
Metropolis Water Act, 1871.

London, August 6th, 1886.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, the whole were found to be perfectly clear, bright, and well filtered.

Altogether, the water supply for the past month has maintained the satisfactory character which it has now exhibited uninterruptedly for some time past. The mean proportion of organic carbon in the Thames-derived supply was 0.140 part in 100,000 parts of the water, as against a mean of 0.152 part in the preceding month's supply.

In carrying out the bacteriological inquiry, of which we gave an introductory notice in our last monthly report, one of our earliest series of experiments, in which we aimed more especially at simplifying the conditions as much as possible, was made with sterilised distilled water, infected with about $\frac{1}{100}$ th of its bulk of peptone-fluid loaded with an active sporeless growth of the splenic fever bacillus. This addition of peptone-fluid to the water operated on, besides furnishing an abundance of the morbid micro-organism which formed the special subject of the experiment, necessarily effected a considerable charging or pollution of the water with animal and other organic matter, besides adding to it an almost insignificant quantity of saline or mineral matter. Calculated from the percentage of nitrogen present in the dry peptone, the proportion of organic nitrogen in the purposely infected distilled water could not have been less than 2 parts in 100,000, or about forty times the proportion commonly met with in the Thames-derived supply of the Metropolis. In so far, accordingly, as the presence of nitrogenous organic matter is concerned, the water experimented on was, as compared with Thames water, in a condition eminently favourable to the continued life and growth of the introduced microbe.

Seven experiments in all were made with distilled water infected as above described, and were set going on seven different days from March 9th to March 24th inclusive. One of the experiments was made in quadruplicate, and the other six in duplicate. Each experiment involved the sowing of from four to twelve tubes of sterilised culture-fluid with the infected water, or a total of more than fifty sowings, and of course an indefinite number of observations, from time to time, of the results of each particular sowing. The infected water was kept at the temperature

of the air of the room, which on different occasions varied from 56° to 59° F. (13·5° to 15° C.). The tubes of culture-fluid sown with the infected water were kept for several days in an incubator at the uniform temperature of 90° F. (32° C.). It was observable, however, that when a development of bacillus in the culture-fluid did not become apparent within from 18 to 24 hours, it did not manifest itself after any longer incubation.

The general result of this series of experiments was as follows:—The culture-fluid, when sown with some of the infected water within two hours of its having been infected, invariably exhibited on incubation an abundant and characteristic growth of the bacillus, from which further growth could be set up indefinitely. The same culture-fluid when sown with the infected water from three to four hours after its infection, furnished irregular results on incubation. Sometimes there was, and sometimes there was not, more or less bacillar growth of the ordinary character; while in some cases what growth there was, much or little, put on a peculiar fluffy appearance, very different from the usual appearance of *bacillus anthracis* culture, and might, it was thought, not improbably (?), possess only an attenuated morbid activity. When the sowing, however, was with distilled water which had been infected five or six hours previously, or from that up to forty-three hours previously—beyond which lapse of time the experiment was not continued—the culture-fluid invariably remained unaffected on incubation, or the addition of the at one time infected water was found to be barren of any results; showing that in the case of distilled water, despite the comparatively large proportion of nitrogenous organic matter added, the introduced bacillus was not able to undergo development, or to maintain its existence for more than a few hours.

The above-described series of experiments made with sterilised distilled water was followed up by a series of

who have inspected it) of hundreds of layers of white and grey shale one above the other, sometimes being separated by small beds of clay of a whitish colour containing rock-salt (or “beds of fossil salt,” as Lyell liked to call it). The extent of this geological formation is very great, extending, as at present discovered, unbroken over 30 square miles of country. The layers of shale are foliated almost like sheets of paper, this being due to the great pressure they have been subjected to during their formation or subsequently. I am given to understand the whole territory in this part of the world strongly resembles the paraffin and salt districts of Galicia. The Servian shales are rich in paraffin and have remained unobserved until about two and a half years ago, but it has been known for “ages” that cattle, birds, and other animals have been in the habit of resorting to these cliffs and eating the clay containing the rock-salt. This paraffin shale is entirely free from bituminous impurities and is of a nearly white colour; it has no odour.

It is very difficult to say what is the origin of the paraffin in these deposits, but most likely it is of vegetable origin*, having been produced from a natural distillation of the old brown coals which abound in the vicinity of the deposits. The author has conducted a series of careful chemical analyses upon specimens of the rocks of this part of Servia.

A sample of the paraffin shale yielded on distillation at 70° C. a semi-solid hydrocarbon; this semi-solid yields, on treating with “benzoline” 1·75 per cent of wax (a solid paraffin) and 0·25 per cent of hydrocarbon oils. What remains are the mineral constituents of the shale plus a carbonaceous matter containing nitrogen. On incineration this residue (contained in the retort) yields 92·04 per cent mineral matters of the original weight of the paraffin shale taken for analysis. The complete analysis stands as follows:—

(I.) Paraffin Shale.

2·00 per cent	{ Semi-solid hydro-carbon distils over at 70° C. }	1·75 per cent wax.
3·02	Water of combination.	0·25 “ { hydrocarbon oils of the C _n H _{2n+2} series. }
2·94	{ Carbonaceous matter containing nitrogen. }	= (yields) 1·18 per cent Ammonia.
92·04	Mineral Matters (Analysis given below).	
100·00		

analogous experiments made with sterilised Thames water, the more or less similar results afforded by which we proposed to give some account of in our next monthly report.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

ON CERTAIN EOCENE FORMATIONS OF
WESTERN SERVIA.*

By Dr. A. B. GRIFFITHS, F.R.S. (Edin.), F.C.S. (Lond. and Paris).
Head Master and Lecturer on Chemistry, School of Science,
Lincoln.

THESE formations (consisting of shale containing paraffin wax and clay) are situated near the River Golabara in the West of Servia. The shale occurs in upheaved cliffs about 200 feet above the surrounding plains. The formations consist (according to the geologists and engineers

II. Analysis of Mineral Constituents of a Servian Paraffin Shale.

Alumina (Al ₂ O ₃)..	..	32·86 per cent.
Iron Oxide (Fe ₂ O ₃)	5·20 “
Magnesia (MgO)	1·26 “
Lime (CaO)	1·21 “
Potash (K ₂ O)	2·17 “
Soda (Na ₂ O)	0·41 “
Silica	56·85 “
Loss	0·04 “
		100·00

The old brown coals of the neighbourhood (which contain more or less rhombic iron pyrites (Marcasite, frequently in rather large macles), gave on analysis:—

	I.	II.
Carbon ..	49·2 p.c.	49·3 p.c.
Hydrogen ..	1·1	1·2
Water (chemically combined) ..	30·2	30·5
Water (hygroscopic) ..	19·5	19·0
	100·0	100·0

* Read before the Geological Society of London, June 23, 1886; communicated by Prof. J. W. Judd, F.R.S., P.G.S., &c.

* See Dr. Griffiths's paper “On the Occurrence of Phenol in *Pinus sylvestris*; A Discovery bearing on the Flora of the Carboniferous

The quantity of ash contained in these coals is between 5 and 7 per cent, and consists chiefly of alumina, lime, magnesia, iron oxide, and silica. Eruptive porphyry and trachytic rocks are plentiful at a distance of five or six miles from the deposits. The shale deposits are of marine origin and of the eocene period. The eruptive rocks just alluded to protude into these deposits and are of a later date than the deposits themselves.

Samples of the eruptive porphyry and trachytic rocks gave on analysis the following compositions:—

(I.) *Eruptive Porphyry.*

Alumina (Al_2O_3).. ..	18.10	per cent.
Iron Oxide (Fe_2O_3)	2.69	"
Manganous Oxide (MnO).. ..	0.82	"
Lime (CaO)..	0.36	"
Magnesia (MgO)	0.12	"
Potash (K_2O)	1.23	"
Soda (Na_2O)	0.16	"
Silica (SiO_2)	75.51	"
	99.99	

(II.) *Trachytic Rocks.*

Alumina (Al_2O_3).. ..	20.82	per cent.
Iron Oxide (Fe_2O_3)	5.03	"
Manganous Oxide (MnO).. ..	0.01	"
Lime (CaO)..	1.98	"
Magnesia (MgO)	0.51	"
Potash (K_2O)	7.03	"
Soda (Na_2O)	3.10	"
Phosphoric Acid (P_2O_5)	0.03	"
Silica (SiO_2)	61.49	"
	100.00	

The clay beds of this part of the world contain large numbers of the genera *Ostrea*, *Cerithium*, *Cyrena*, *Nautilus*, and *Voluta*; with the fossil remains of the vertebrata which lived in the Eocene Seas, &c.

These remains consisted principally of the Teleostean and Placoid fishes, the former predominating considerably. I may say, in passing, *no* horned hoofed mammals have so far been discovered in these Servian deposits corresponding to Professor Marsh's *Dinocerata* of the Eocene deposits of America.

It may be that during the Eocene period in Europe the climatic conditions were not suited for the thirty or more species of Eocene *Dinocerata* mammals which lived in the New World during these geological times.

The clays of the districts in question from which the shales were originally formed contain innumerable microscopic siliceous shells of marine Diatomaceæ with calcareous shells of Foraminifera (principally of the genus *Nummulites*); and it is supposed to be similar to the ooze now forming at the bottom of the Atlantic and other oceans. From the structure of the formations and other considerations it is thought that in the limestone rocks which underlie these shale deposits, rock-salt and petroleum wells will be found; and it is highly probable that all the deposits of the district are more or less of organic origin (limestones, shales, brown-coal, paraffin, &c.) or in the words of the poet Byron:—

"The dust we tread upon was once alive."

Further, the engineers who have inspected the district say that the shale can be extracted by open quarrying at "the cost of a few pence per ton"; and that in distilling the shale on the spot now that gas-retorts are in use the shale itself can be utilised as fuel. These formations are situated in easy access of the Rivers Sava and Danube.

Epoch and the Formation of Petroleum," CHEMICAL NEWS, vol. xlix., p. 95; *Berichten der Deutschen Chemischen Gesellschaft* No. 6, 1884 p. 171; and *Chemiker Zeitung*, vol. viii., p. 342.

EMBOLITE: ITS COMPOSITION AND FORMULA.

By CUTHBERT WELCH.

IN the CHEMICAL NEWS, vol. liii., p. 99., Mr. J. M. H. Munro gives an analysis of embolite from St. Arnaud, Victoria, claiming for the mineral, on the strength of this analysis together with one by Mr. C. Wood, the simple formula $\text{AgCl}.\text{AgBr}$. During a mineralogical study of the ores of silver my attention has once more been drawn to the composition of this ore, a subject which has on several previous occasions interested me. Can it be regarded as a single mineral with rather large variations in composition, or rather as an indefinite mixture of hornsilver and bromite? The latter view appears to me to be the more probable, for of 14 analyses (being all of which I have any record) 4 agree closely with $\text{AgCl}.\text{AgBr}$, 2 with $5\text{AgCl}.\text{AgBr}$, 7 call each for a separate formula, and only 1 agrees with the equimolecular formula $\text{AgCl}.\text{AgBr}$, although this is usually quoted as representing the composition of embolite. It is also worthy of notice that the specimen yielding this simple formula is from Victoria, whilst no single specimen from Chili has agreed with it, although by far the greatest amount of this ore is derived from the latter country.

In proof of the above I append these 14 analyses arranged according to their composition, with the authority upon which I quote each:—

I. $\text{AgCl}.\text{AgBr}$.

C. Wood, from St. Arnaud. ("Goldfields and Mineral Districts of Victoria," by R. B. Smyth, F.G.S., p. 411. 1869).

				Theory.
AgCl	43.23			43.288
AgBr	56.77			56.712
	100.00			100.000
	Or,			Or,
Ag	65.14			65.159
Br	24.16			24.136
Cl	10.73			10.705
	100.03			100.000

II. $\text{AgCl}.\text{AgBr}$.

F. Field, from Chanarcillo, Chili. (*Quarterly Journal of Chemical Society*, x., p. 239. 1858). Very dark green, sometimes of a rich purple colour.

				Theory.
AgCl	20.52			20.297
AgBr	79.48			79.703
	100.00			100.000
	Or,			Or,
Ag	61.07			61.063
Br	33.82			33.916
Cl	5.00			5.021
	99.89			100.000

III. $2\text{AgCl}.\text{AgBr}$.

F. Field, from Chanarcillo, Chili. (*Quarterly Journal of Chemical Society*, x., p. 239. 1858). Pale green colour.

				Theory.
AgCl	60.43			60.422
AgBr	39.57			39.578
	100.00			100.000

	Or,	Or,
Ag	68'22	68'212
Br	16'84	16'841
Cl	14'92	14'947
	<hr/> 99'98	<hr/> 100'000

IV. 2AgCl.3AgBr.

W. von Beck, from silver mines in the Troitzer Bezirk, Orenberg. (*Fahrbuch für Mineralogie*, 1876, p. 165). In minute octahedrons and in thin crusts.

		Theory.
AgCl	33'17	33'725
AgBr	66'83	66'275
	<hr/> 100'00	<hr/> 100'000
	Or,	Or,
Ag	63'35	63'455
Br	28'44	28'202
Cl	8'21	8'343
	<hr/> 100'00	<hr/> 100'000

(To be continued).

NOTICES OF BOOKS.

The Techno-Chemical Receipt Book. By WILLIAM T. BRAUNT and WILLIAM H. WAHL, Ph.D. (Heid.) Philadelphia: Henry Carey Baird and Co.; and London: Sampson Low, Marston, Searle, and Rivington.

THE title of this book is rather misleading, the contents being of a much more general character than we should expect. The part which is headed "Chemical and Techno-Chemical Expedients, Preparations," comprises only five pages out of a total of 460, and amongst them we find a receipt to "thaw frozen ground" by means of putting snow and unslaked lime over it; this seems hardly to come under the above named heading. There is, however, a very large amount of exceedingly useful information in the book, the receipts comprising a wide range of subjects, such as making artificial eyes, cleaning gloves, making fulminates, poisoning rats, mixing paints, and many more of as varying a character. The principal subject headings are all in alphabetical order, thus rendering it an easy matter to find anything that is in the book, while there is at the end a copious index. The utility of such a book of reference for nearly every trade is beyond all question, and we wish the authors every success.

CORRESPONDENCE.

DISCUSSION ON THE NATURE OF SOLUTION.

To the Editor of the Chemical News.

SIR.—It may, perhaps, be convenient to those chemists who have announced their intention of joining in the proposed Debate in Section B at the approaching meeting of the British Association that, having accepted the invitation of the President to open the discussion, I should indicate briefly the general nature of the subjects upon which I shall offer some remarks, and the order in which I shall probably take them.

After a historical sketch of the theories which have been framed with the object of explaining the constitution of saline and other solutions, the phenomena of solution will be dealt with somewhat as follows:—

Thermal and volume changes occurring in the act of solution and their mutual relations. How far and under what circumstances are thermal and volume changes to be considered as indicating chemical change?

The molecular volumes of salts in solution. The specific heat and vapour pressures of salt solutions. The relation of solubility to molecular volume, to fusibility, and to the composition of the liquid.

Action of solids, and especially of porous bodies, on solutions.

Phenomena of supersaturation.

What is chemical combination, and is there any criterion by which it may be distinguished from adhesion or mechanical combination.

In consequence of the very wide reaching character of the subject it will not be possible to take up the question of solution except as relating chiefly to solids, and especially salts, in water. For the same reason I cannot fully discuss the phenomena of absorption spectra, nor generally the action of solutions upon light, but I hope some of those chemists who have worked on this part of the subject will be present and will give us the benefit of their experience.

There will of course be a great number of questions incidentally touched upon in my opening, which may well form the basis of remarks from other speakers, such as:—

How is saturation to be explained, *i.e.*, why is there generally a limit to solubility?

Is there any general connection between solubility and atomic weight in a series of compounds in which only one constituent varies?

What becomes of water of crystallisation when a salt containing water is dissolved in water?—I am, &c.,

WILLIAM A. TILDEN.

The Mason College, Birmingham,
August 12, 1886.

MAGENTA *v.* FUCHSINE.

To the Editor of the Chemical News.

SIR,—I am surprised and sorry to find that my protest against the kakophonous and un-English term "fuchsine" should incur the disapproval of Mr. A. H. Allen. I do not deem it necessary to take up your space by recapitulating all the objections to fuchsine. In the first place it is misleading. From analogy, when we see the termination "ine" appended to the name of a plant, or part of such name, we expect a proximate principle obtained from the plant in question. Hence such names as fuchsine, azaleine, roseine, geranosine, helianthine, &c., are to be condemned. It would not be difficult to find among fuchsia flowers twenty tones which could not be dyed with magenta at all, especially without the admixture of other colouring-matters. Lastly I must point to the custom of trade. Dyers, tissue printers, and the authors of works intended for their use, call the commercial salts of rosaniline "magenta," and if they mention "fuchsine" at all make it rank as a mere synonym. I may give as instances Benedikt and Knecht's "Chemistry of the Coal-Tar Colours," Hummel's "Dyeing of Textile Fabrics," Grace-Calvert's "Dyeing and Calico Printing," &c. If we are to use fuchsine in preference to magenta we may as well discard the English names cudbear, turmeric, and annatto in favour of persio, curcuma, and Orleans.—I am, &c.,

YOUR REVIEWER.

On the Hydrates of Zinc Chloride.—R. Engel.—There exist three hydrated zinc chlorides containing respectively 3 and 2 mols. of water to 1 mol. of the anhydrous chloride, and 3 of water to 2 of the anhydrous compound.—*Bull. de la Soc. Chim. de Paris.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 5, August 2, 1886.

On the Displacement of Ammonia by other Bases and on its Determination in Soils.—MM. Berthelot and André.—The authors consider it established that ammonium-magnesium phosphate is not appreciably decomposed at 100° in an hour by calcined magnesia, and very imperfectly by lime, the latter fact having been previously observed by Boussingault. Hence magnesia cannot be safely employed in the determination of ammonia in the analysis of soils and organic products containing insoluble ammoniacal double salts. Certain derivatives of the aldehyds are in the same case, and there is reason to fear the same thing for the ammoniacal salts formed by humic acid by its congeners. As to allowing the use of magnesia to be preceded either by washing the soil with dilute nitric acid until an incipient acid reaction is perceived, as M. Schloësing not long ago proposed, or by dissolving the soils in pure hydrochloric acid, a new process which he recommends in his last memoir, these expedients suggest reservations which the present authors still maintain.

The Determination of Ammonia.—T. Schloësing.—The author has shown in his paper of July 26 that, by distillation over magnesia, the total ammonia can be extracted from the solution of ammonium chloride or from that of ammonium-magnesium phosphate. To complete his demonstration he has caused magnesia to act upon double ammoniacal salts, especially the chlorides into which enter magnesium and zinc. He has accordingly operated upon five double salts, the ammonium-sulphates of magnesium, zinc, and copper, and the ammonium chlorides of magnesium and zinc. He finds that in all these cases the use of magnesia for the liberation of ammonia may be continued with safety.

Separation of Arsenic, Antimony, and Tin.—Ad. Carnot.—Will be inserted in full.

Formation-Heat of Amorphous Selenides.—C. Fabre.—In general the formation-heat of the selenides prepared at high temperatures is equal or slightly lower than that of the corresponding precipitated sulphides. As for the precipitated selenides, their comparison with the corresponding sulphides shows that the difference between the formation-heats of the metallic sulphides and selenides is less than the difference between the formation-heats of the alkaline sulphides and selenides.

Composition of the Portion of Suint Soluble in Water.—E. Maumené.—The author has hitherto published a small part only of the researches which he carried on in concert with the late Victor Rogelet. The memoir laid before the Academy by M. Buisine induces him to publish one of his results. He has studied the volatile products of the pyrogenous decomposition of the mixture of potassium salts extracted by water from suint. Among these he has isolated a new product, dienic ether, to which he assigns the formula C_4H_4HO . It is absolutely colourless, very mobile, boils at 36° at a pressure of 761 m.m., and has the specific gravity 2.7. It is derived from the pyrogenous decomposition of potassium lactate.

Journal für Praktische Chemie.
New Series, Vol. xxxiv., Part I.

Researches from the Chemical Laboratory of the University of Leipzig, Communicated by E. von Meyer.—These communications consist of a paper by

V. K. Voigt on the action of primary aromatic amines upon benzoin and a memoir by A. Pfungst on the action of nitromethan upon certain chlorhydrines.

Contributions to the Chemistry of Manganese and of Fluorine.—O. T. Christensen.—Nicklès has formerly stated that manganese tetrachloride is formed by the action of ether containing hydrochloric acid upon manganese peroxide. The author has succeeded in showing that the ethereal solutions with which Nicklès operated contain only Mn_2Cl_6 . The action of hydrofluoric acid is similar. The atomic weight of fluorine has been found to be 18.94 ($H=1$) or 18.99 if $O=16$. On the electrolysis of a solution of Mn_2F_6 in hydrofluoric acid there is formed at the positive pole, if it offers a large surface, abundance of permanganic acid. The reaction is so well marked that even traces of a salt of manganese, if dissolved in aqueous hydrofluoric acid and exposed to the current, show almost instantly the violet-red colour of permanganic acid at the margin of the liquid. The reaction succeeds best if the platinum capsule with the liquid is made to serve as the positive electrode. On heating the higher manganese double fluorides, especially that of the double sodium salt, in a platinum tube in dry pure oxygen or nitrogen, there appears at first a little of another gas, possibly fluorine, which liberates iodine from solid potassium iodide and bromine from potassium bromide. Afterwards the tube becomes porous and the combustion-products of the gas penetrate the pores, forming hydrogen fluoride.

Arabonic Acid and a Sugar formed from Lichenine.—R. W. Bauer.—The author has previously shown that arabonic acid is formed on oxidising arabinose with bromine, and that it is distinguished from gluconic acid by the solubilities of its cadmium salt. The composition of arabonic acid is represented by $C_6H_{10}O_6$. Its melting-point is 89°. The sugar obtained from lichenine immediately after solution showed a polarising power of about +50°; a day subsequently, as the mean of several observations, +28.5°.

Condensation of Formaldehyd.—O. Loew.—Some time ago the author reported on the formation of a sugar from formaldehyd, the condensation process being mediated by calcium hydroxide. The observation that the condensation is possible in a simply watery solution may be of some interest in vegetable physiology. The condensation ensues the more readily the more dilute is the formaldehyd. A sugar was obtained on boiling a $\frac{1}{2}$ per cent solution of formaldehyd for twelve to fifteen hours with granulated zinc (or preferably granulated tin) in a cohobator. In this latter case there is a catalytic action concerned. The quantity of tin must be considerable, which speaks in favour of surface action. Neither copper nor mercury can be used in place of tin. This process has evidently the greatest resemblance to those which occur in plants. Here also the question is often solely a transfer of conditions of movement (from the living protoplasm) to the material selected for syntheses or scissions. The great physiologist Ludwig was perfectly right when he said: "A large portion of physiological chemistry may easily become a part of catalytical chemistry."

Reply to H. F. Stohmann.—Julius Thomsen.

Conclusion of the Polemics with H. Thomsen.—F. Stohmann.—A discussion on Prof. Thomsen's method of conducting his thermo-chemical experiments, which seems in danger of degenerating into a quarrel.

Die Chemische Industrie.
Vol. ix., No. 5, May, 1886.

The Influence of the Presence of Arsenic on the Specific Gravity of the ordinary Oil of Vitriol of Commerce.—Dr. R. Kissling.—Whilst a pure sulphuric acid containing 93.64 per cent. of monohydrate has the

sp. gr. 1.8360, a sample of arseniferous acid, containing 93.60 per cent. of the monohydrate and 0.254 of arsenious acid marked 1.8413.

Justus Liebig's Annalen der Chemie,
Vol. ccxxxiii., Part 3.

Researches on the Physical Properties of Liquid Compounds.—These investigations include memoirs on the boiling-points and the specific volumes of the normal esters of fatty acids, by Dr. R. Gartenmeister, and on atomic volume and specific volume by W. Lossen.

Communications from the Chemical Institute of the University of Bonn.—This consists of the first part of a memoir by R. Anschütz and E. Romig on the action of nitric acid upon unsymmetrical diphenylethan.

Communications from the Chemical Laboratory of the University of Moscow.—These comprise a paper by P. Orloff on hexylglycerin from allyl-dimethyl-carbinol, and a memoir by A. Siwoloboff on the dichlorhydrine of mannite and its reduction.

Determination of the Carbon, Hydrogen, and Nitrogen of Organic Compounds by a Single Combustion.—Paul Jannasch and V. Meyer.—The combustion of the sample is effected in the ordinary manner in a combustion tube with copper oxide and a layer of copper spirals. The tube is connected in the front in the ordinary manner with a calcium chloride tube, a potash apparatus, and a special arrangement for collecting the nitrogen. At the back it is drawn out to a point. The entire combustion is executed in an atmosphere of pure oxygen, which, before the commencement of the operation, has entirely expelled the air out of the apparatus, just as this is done in Dumas's method by means of carbonic acid. But, whilst in the latter case the nitrogen gas is collected over potash-ley, the authors collect it over a solution of chromous chloride, which is an excellent absorbent for oxygen. The current of pure oxygen was obtained from a mixture of potassium dichromate and permanganate.

Vol. ccxxxiv., Part 1.

On Derivatives of the Chlorinised Paranitrophenols.—A. Kollrepp.—This extensive memoir does not admit of useful condensation.

Communications from the Laboratory of Prof. J. Wislicenus.—These consist of a memoir, by C. Rach, on the action of nascent hydrocyanic acid upon acetsuccinic ester, and a paper by C. A. Bischoff and C. Rach on hydro-pyrocinchonic acid.

The Aromatic Hydrocarbons of the Caucasian Mineral Oil.—W. Markownikoff.—The raw material used was the naphtha from the Balachary plain, in the peninsula Apscheron, near Baku. Among the products obtained in the fractions boiling between 85° and 250° are benzol, toluol, isoxylol, pseudocumol, mesitylene, durol, isoduro, diethyltoluol and its isomers, and at least four hydrocarbons of unknown structure. The portion boiling at 210° contains only homologues of the benzol series. Above this temperature there occur compounds of the series $2nH_{2n}-8$, and from the higher distillates there are obtained compounds still poorer in hydrogen. The chemical nature of these latter has not been accurately determined, but those compounds of the series $C_nH_{2n}-8$, $C_nH_{2n}-10$, and $C_nH_{2n}-12$, which the authors had in their hands, can certainly not rank with the so-called non-saturated hydrocarbons, whose representatives are found in styrol, phenylacetylene, &c. The inability of the hydrocarbons obtained to unite directly with halogens leads the authors to suppose that they are representatives of quite new series.

Investigations on the Pyridin-Carbonic Acids.—W. Roser.—The author has subjected chenolic and nicotic acids, pyridin-tricarbonic and cinchomeronic acid to the

action of methyl-iodide. He finds that all these four acids undergo modifications even at 100° in presence of methylic alcohol. Nicotic acid alone leads to methyl ammonium iodide; chinolic acid splits off carbonic acid and yields nicotic methyl-iodide. The experiments with pyridin-tricarbonic acid and cinchomeronic acid led to the synthesis of apophyllenic acid.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xiv., No. 1, July 1, 1886.

Wine of Rice.—M. Busgen.—This strongly alcoholic liquor is in great esteem in all the eastern portion of Asia. Its fermentation is effected by a fungus known as *Aspergillus orizæ*.

Determination of Acid Magenta, Bordeaux Red, and Soluble Red in Wines.—J. Bellier.—The author states that his experiments are quite conformable to those of M. Sambuc. His method reposes on the use of a mixture of mercuric acetate, dry and powdered, and of calcined magnesia; 84 parts of the former ingredient, with 16 of the latter, gave the best results. Fifty c.c. of the wine were raised to a boil in a porcelain capsule; the powder was added, and the liquid, after stirring, was filtered into a 100 flask containing 2 c.c. of sulphuric acid with a little water. The precipitate was then washed so as to make up the filtrate to 100 c.c. The liquid was then compared colorimetrically with an aqueous solution of acid magenta. The determination of Bordeaux red and soluble red is effected in a similar manner, but as a certain quantity of the colouring matter is fixed energetically upon the filter it must be dissolved with alcohol, or preferably in ammoniacal alcohol. By the use of this method 3000 hectolitres of wine, fraudulently coloured, have been seized in one year at the various railway stations in Lyons. The author announces that he will shortly publish a method founded on an entirely different principle and applicable to a great number of colours.

On Petroleum-Ether.—V. Péquart.—The only safe method of ascertaining the purity of this product is distillation of a rather large quantity in the water-bath, raising the temperature gradually to 60° and 65°, without exceeding this point. If the receiver is then changed and the heat raised to 70° there passes over a colourless liquid of a different odour and of a slightly acid reaction. If, when nothing more passes over, the temperature is raised to 85°–90° the product of the retort becomes black and separates on cooling into two strata. The upper layer is yellowish, transparent, and slightly acid. The lower is dark brown and strongly acid.

The Organic Matter in Potable Waters.—M. Fauvel.—The author's experiments have been made according to Koch's method, which rests on the double property of gelatin as being an excellent culture-medium for bacteria, and being liquefied by the bacteria of putrescent animal matter. It was observed that the water of the canal of l'Ourcq contains fewer colonies than that of the Vanne, but yet these colonies liquefy the gelatin more rapidly. The results have been checked by chemical analysis, the organic matter being determined by means of potassium permanganate.

Resistance of Microbia to the Heat of Stoves.—Dr. Grancher.—Moist steam at a pressure of 106 centimetres was found more effective than dry steam.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xx., Part 5.

The Melting-point of Ice under Pressures Lower than that of the Atmosphere.—B. J. Goosens.—To decrease in pressure corresponding to the atmosphere there corresponds a rise of temperature = 0.0066°.

Bulletin de la Société Chimique de Paris.

Vol. xlv., No. 12, June 20, 1886.

Action of Oxygenated Water upon the Oxides of Chrome.—M. Martinon.—When hydrogen peroxide reacts upon chromic acid in an acid liquid there appears the blue colouration characteristic of perchromic acid. Gradually the blue colour disappears and a salt of chromium sesquioxide remains whilst oxygen is liberated. Perchromic acid is, therefore, an addition-product formed by chromic acid and hydrogen peroxide and having the composition $\text{Cr}_2\text{O}_7\text{H}_4$. This addition-product is blue in presence of acids and of a dirty red in neutral liquids. In this latter case the decomposition is more rapid. If oxygenated water is allowed to act upon chromium dioxide, as prepared by Schweitzer's process, there is formed a chromate without escape of oxygen if the liquid is alkaline. In a neutral liquid the reaction is excessively slow, but ultimately there is formed a little chromic acid. In an acid solution oxygen is given off and there is formed a salt of chromium sesquioxide. In all these cases chromium dioxide behaves absolutely like a chromate of chromium sesquioxide. In neutral or acid liquids chromium sesquioxide does not react with oxygenated water, but in an alkaline medium there is immediate formation of a chromate. This means may serve for detecting salts of chromium; it gives even in very dilute solutions of the chromic salts, especially if slightly heated, very distinct results, and may be utilised in analysis.

Little Known Cause of the Corrosion of Steam Boilers.—D. Klein and A. Berg.—The authors show that cane sugar, inverted sugar, and decoction of malt attack iron strongly, forming an acid product. Glycerin and mannite have no action. Zinc is strongly attacked with a copious escape of hydrogen. Copper, tin, and aluminium are not attacked. If lead or cadmium is heated in a sealed tube to 120° to 125° with a concentrated solution of sugar it forms abundance of a brown amorphous body belonging to the class of those ill-defined bodies known as carameline, caramelane, &c. The liquid has a strong acid reaction and contains traces of lead or cadmium.

Observations on the Above Memoir.—M. Lodin.—The influence of saccharine solutions upon boiler-plating was discussed in a report presented July 2nd, 1878, to the Central Commission of Steam Engines, by M. Luuyt, and was published in the *Annales des Mines*, Series 7, vol. xiv. M. Lodin has also shown in a note communicated to the Academy of Sciences, July 26, 1880, that metallic iron reacting upon water in sealed tubes at temperatures a little exceeding 100° , gives rise to a liberation of hydrogen, accompanied by an attack of the iron. The presence of certain organic matters, such as starch and hematoxylin, intensifies the action.

Comparative Reactionary Aptitude of the Halogenous Derivatives of Sulphur.—W. Spring and A. Lecrenier.—The conclusions reached in this memoir are that for sulphur chlorides and bromides the quantity of free chlorine or bromine is so much the greater as the quantity of the substance employed differs more widely from S_2Cl_2 or S_2Br_2 . If this fact is connected with the phenomena of dissociation made known by Michaelis, we are led to seek its origin in a true dissociation of these compounds. The affinity of chlorine for sulphur appears to be 9.43, and that of bromine 7.37 times greater than that of iodine; all other conditions being equal. The halogenous derivatives cannot in any manner be assimilated to alloys. They are not the result of the dissolution of a free portion of their elements in another combined portion, but their composition varies according to the laws of dissociation.

Direct Chlorination of Methyl-benzoyl.—H. Gautier.—In the action of chlorine upon methyl-benzoyl we obtain simultaneously the three chloro-substitution derivatives in the methyl group. But this process enables us to obtain only the mono-chloro product in a state of

purity. The action of the chlorine must not be too prolonged, since this product is very soluble in the mixture formed by the bi- and tri-chloro derivatives.

On Effluviography.—D. Tommasi.—The substance of this brief communication has already been extracted from the *Comptes Rendus* (see CHEMICAL NEWS, vol. liii., pp. 179, 191).

MISCELLANEOUS.

A Reaction of Atropine and its Kindred Alkaloids.—A reaction observed by Gerrard was described in a former volume of *Zeitschrift*. Schweissinger has subjected it to a renewed examination and finds Gerrard's observation fully confirmed. He has also treated a number of other alkaloids (which Gerrard had not examined) in the same manner, which produced a red precipitate with atropine, i.e., he covered 0.5 to 1 m.g. of each with an alcoholic solution of mercuric chloride and applied a gentle heat. Arbutine, condurangine, and sparteine gave no precipitate; cocaine yielded a white precipitate, but only in very concentrated solutions. Scopolamine gave a yellow precipitate. The behaviour of hyoscyamine and homatropine is particularly interesting. If 1 m.g. of the former is covered with 2 c.c. of the 5 per cent alcoholic solution of mercuric chloride no precipitate appears, but if only two drops of the solution are used the precipitate comes up on gently warming, just as with atropine, and does not disappear on the addition of more of the mercuric solution. Homatropine, which with sulphuric acid and sodium nitrite behaves exactly like atropine, yields with alcoholic mercuric chloride no precipitate at all, is produced if the solution is dilute, but in a concentrated solution a white precipitate, which disappears on the addition of a further quantity of mercuric chloride; no red precipitate appears. The reaction is suitable for quantitative determinations; it applies only to the alkaloid itself and not to its salts. The caution is given that inorganic basic bodies, such as calcium and magnesium hydroxides, produce the very same precipitates.—*Zeitschr. f. Anal. Chem.*, xxv., Part 3.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Silver Plating.—Will some correspondent be kind enough to give me through your valuable paper a reliable "receipt" of a solution (silver) for electro-plating. I have made up several from text-books, but have not as yet got one to work satisfactorily. Two Smee's batteries should work it, should they not?—G. T. CRAVEN.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1396.

NOTE ON THE USE OF SOAP SOLUTION.

By GEO. E. R. ELLIS, F.C.S.

IN working out the hardness of a water some analysts are wont to proceed thus: They make two determinations, in the first the soap solution is run in boldly, 5 c.c. or so at a time, and the hardness is approximately ascertained, while in the second the soap solution is run in at once almost up to the point of saturation, and is then carefully adjusted drop by drop.

In order to test the correctness of this mode of procedure the hardness of waters containing various salts in solution was determined under different conditions of treatment. Thus:

(1.) The soap solution was added slowly (1 c.c. or less at a time) and the sample was shaken for 10 seconds after each addition. (Call the number thus obtained A.)

(2.) The soap solution was added in bulk (almost up to the point of saturation, A), the mixture was shaken for 10 seconds, and the soap solution was then added drop by drop, until a permanent lather was obtained. (B.)

(3.) Experiment 2 was repeated, but the sample was allowed to stand for five minutes after the first shaking. (C.)

(4.) Experiment 3 was repeated, but the sample was allowed to stand for 15 minutes after the first shaking. (D.)

(5.) The soap solution was added almost up to the point of saturation (as in 2), the mixture was then shaken vigorously for 10 minutes, and the final point of the reaction then obtained by adding the soap solution drop by drop. (E.)

A large number of experiments were performed, but the data given in the following Table will be sufficient to show that the mode of procedure which some chemists employ is not calculated to give accurate results.

A glance at the Table will show that the numbers obtained under the head A are always less than those under C, and still less than those under B. Also we see that the more thoroughly the soap solution is made to mingle with the water the more nearly does the reading obtained approach to that given under A.

When we consider, too, that everything was done to make the experiments as strictly comparable as possible,

and that the shaking in every case was continued for the same time and as nearly as possible in the same manner and degree, these numbers seem to indicate (1) that the mechanical act of shaking is more effective in the case of water containing calcium salts than in those containing magnesium salts, and (2) that the harder the water, within certain limits, the greater seems to be the percentage reduction in the quantity of soap solution required when the sample of water is vigorously shaken.

In the face of these results, therefore, in determining the hardness of a water, the soap solution should be added in *small* quantities (1 c.c. or less) at a time, and the mixture be well shaken after each addition.

I am aware that similar advice has been given by other chemists, but I have not been able to meet with the account of any experiments which bear out the value of the precept.

10, Colville Road, Bayswater, W.

THE SEPARATION OF ARSENIC, ANTIMONY, AND TIN.

By AD. CARNOT.

THE reactions of the alkaline hyposulphites in presence of various acids, upon which the author has founded the separation of a number of metals, may also serve for the separation of tin.

If, into a hydrochloric solution of arsenious or arsenic acid, heated to about 100°, we pour a solution of hyposulphite, there appears at first a white turbidity, due to precipitated sulphur, and then a yellow colouration produced by arsenic sulphide. The same phenomenon occurs in a solution acidified with oxalic acid. But the precipitation is always incomplete on account of the liberation of a certain quantity of sulphurous acid, which tends to bring back the sulphide to the state of arsenious acid. If we beforehand add to the liquid a solution of sulphurous acid, or of an alkaline disulphite, there is no longer formed a yellow precipitate, the sulphur deposited being quite exempt from arsenic. Under the same circumstances the precipitation of antimony oxysulphide is retarded, but still takes place completely. We have thus an easy means of separating arsenic and antimony. To the hydrochloric solution of the two substances it is sufficient to add ammonium oxalate (or, in the absence of tin, ammonium tartrate) and water; then hyposulphite in a quantity proportionate to the antimony; and, lastly, a little sulphurous acid or alkaline bisulphite, and raise to a boil. When the liquid becomes clear, and when an addi-

No. of c.c. of Soap Solution required to produce a Permanent Lather under Different Conditions of Treatment of the Sample of Water.

Sample.	A.	B.	C.	(B-A).	(B-C).	Percentage reduction on shaking for 10 minutes.
I. Containing Mg and Ca salts, the latter in larger quantity	11.8	13.05	—	1.25	—	
II. Containing Mg and Ca salts, the latter in larger quantity	10.9	12.15	—	1.25	—	
III. Ditto, but in different proportions ..	11.47	12.73	12.53	1.26	0.2	
			D		(B-D)	
IV. Ditto	12.75	14.15	13.84	1.4	0.31	
			E		(B-E)	
V. Ditto	12.7	14.1	13.4	1.4	0.7	50
VI. Containing Mg salts only	13.18	14.74	—	1.56	—	
VII. Ditto	13.5	15.0	14.1	1.5	0.9	60
VIII. Ditto	11.64	13.0	12.37	1.36	0.63	46.3
IX. Ditto	10.05	11.36	10.73	1.31	0.63	48.1
X. Ditto	14.2	16.6	15.14	2.4	1.46	60
XI. Containing CaCl ₂ in solution	10.44	11.47	10.82	1.03	0.65	63
XII. Containing CaCl ₂ in solution	10.58	11.7	10.97	1.12	0.73	65

(1 c.c. of the solution = 1 grain of CaCO₃ per gallon).

tion of hyposulphite or of hydrochloric acid no longer produces a white milkiness, it is filtered. We have then, on the one hand, the red precipitate of oxysulphide, in which the determination of the antimony is completed, and, on the other, a solution of arsenious acid, in which the arsenic is easily estimated. For this purpose there is added a large excess of hydrochloric acid; the liquid is heated until the sulphurous acid is expelled, and there is introduced a current of sulphuretted hydrogen, which determines the complete precipitation of arsenic sulphide. The arsenic is re-dissolved by peroxidising it with *aqua regia* or sodium hypobromite, and the determination is completed by one of the known methods. This method of separating arsenic and antimony finds numerous applications in the analysis of ores, and of other minerals in which these two substances are both present.

It is very rare, on the contrary, to find tin along with antimony in natural products, but the two metals are often associated in industrial alloys. We find there also sometimes arsenic, but in small quantities only, and generally in consequence of an impurity in the constituent metals. If all three are found together, the arsenic being in small quantity only, then after having dissolved in an *aqua-regia* (in which the hydrochloric acid is in excess) either the alloy itself or the mixed sulphides, previously separated from other metals by means of ammonium hydrosulphate, we separate first the antimony, as described above in the state of oxysulphide, taking care to prevent the precipitation of the tin and arsenic by means of oxalic and sulphurous acids. The liquid is then raised again to a boil, with a decided excess of hydrochloric acid, and into the almost boiling liquid there is passed a current of sulphuretted hydrogen. The quantity of arsenic being supposed to be small, its complete precipitation is effected if the gas is passed for a few moments. The liquid is kept hot as long as an odour of sulphuretted hydrogen is perceptible, and the formation of tin sulphide is prevented with almost absolute certainty. Nevertheless, for security's sake, the deposit which is slowly formed at the bottom of the flask is treated with a little hydrochloric acid, so as to re-dissolve any tin which it may contain. The residue is collected on a small filter, washed, and dissolved while still moist, in a few c.c. of hot *aqua regia*. The arsenic acid is then estimated as an ammonium-magnesium double salt, or by means of the Marsh apparatus.

The tin remaining alone in solution may be precipitated as sulphide and determined by the ordinary methods.—*Comptes Rendus*, ciii., p. 343.

SPECTRUM OF THE NEGATIVE POLE OF NITROGEN:

GENERAL LAW OF THE DISTRIBUTION OF RAYS IN THE BAND-SPECTRA.

By H. DESLANDRES.

THE first portion of this memoir is specially reserved for the spectrum of the negative pole of nitrogen. The other part is devoted to a law of the distribution of rays which appears distinctly in the bands of the negative pole, but which appears general and common to all band-spectra.

The spectrum of the negative pole of nitrogen is, according to Angström, the only spectrum of any known body found in the Aurora Borealis. But this relation has been denied, as it rests only on the approximations of the wave-lengths.

The author proposes to compare directly by photography the two spectra placed in juxtaposition in the field of the spectroscop, and in the first place he has studied only one of them, the spectrum of the negative pole.

This spectrum appears especially strong in the negative part of the nitrogen tubes at ordinary pressures, and in the entire spark at very low pressures. In the luminous

region, the only one studied hitherto, it is accompanied by faint traces of positive bands; but in the ultra-violet region it is only prolonged by a small number of bands, and is in a manner drowned among the strong and numerous positive bands.

General Law of the Distribution of the Rays.

The rays of the band $\lambda 391$ are distributed according to the following simple law: the intervals from one ray to the following, calculated in numbers of vibrations or the inverse numbers of the wave-lengths, are approximately in arithmetical progression. We may, in fact, form an arithmetical progression such that the difference between any interval of the band whatever and the corresponding term of the progression may be inferior to the ratio.

An analogous relation has been already pointed out by Piazzzi Smyth and Herschel among sixteen rays of the green band of carbon monoxide, but it has been presented by them as an isolated fact. But this simple law appears general, and the author has verified it, almost in the same manner, with some secondary deviations for all the bands which he has been able to resolve into fine rays. The structure is in general much less simple, for most frequently the bands are formed not by a single series, but by several arithmetical series, equal, superimposed, and entangled one with another. The number of series is the same for the bands of the same origin. The author enumerates here the bands which he has studied from this point of view.

The other bands of the negative pole; the bands of the second positive group of nitrogen, which present each three equidistant arithmetical series; the bands of the third group from the positive pole of nitrogen (from $\lambda 300$ to $\lambda 200$), with three or four arithmetical series; the bands of cyanogen, with at least one series; the telluric bands $A B \alpha$, which present each at least one series; the emission bands of watery vapour, which present at least four arithmetical series arranged in groups of two, each such group having the aspect of the bands $A B \alpha$; one band of the combustion of coal-gas, near H, which appears lined with a similar but weaker band. It differs from the foregoing by the following features:—The ratio is greater, and the rays nearest to each other are not the most intense. This last peculiarity is shown still more distinctly in the violet band of the hydrocarbons.

In short, if we consider the great number and the different origins of the bands enumerated, this law appears general, and it is verified for the totality of the rays of one and the same band, in spite of certain irregularities or perturbations manifested by an oscillation of the series of intervals around the corresponding arithmetical series. In general a variation in the intensity of the rays appears accompanied by a variation of the intervals with regard to the progression.

In future, therefore, a band may be defined by the number and the dispersion of its component rays, by the position and the number of a ray of one series, and by the ratio of the progression. The number of series and the ratio are especially characteristic elements.

But the law enounced leads to the following consequence:—If we give to a ray of the series the number 1, and the numbers 2, 3 . . . n to the following rays, the interval between the ray n and the ray 1 is approximately represented by the binomial—

$$\frac{r}{2}(n-1)^2 + s(n-1),$$

r being the ratio of the progression. Moreover we may select another origin and give another number to the ray which is at first the ray 1, so as to render the coefficient small, and at most equal to $\frac{r}{2}$. The intervals

between the origin and the successive rays are then almost proportional to the squares of whole numbers. The foregoing results will be developed in a more extensive memoir.—*Comptes Rendus*, ciii., p. 375.

VERIFICATION OF THE CALCULATION OF THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 89.)

X. Relation between Silver and Chloride of Potassium, γ 14—26.

Chloride of Potassium.	Equivalent in Silver.		Ag : KCl = 100.		Average.
	Saline Limit.	Silver Limit.	Saline Limit.	Silver Limit.	
7.08551	10.24160	10.2606	69.18362	69.05551	69.11956
7.07006	10.21920	10.23820	69.18408	69.05570	69.11989
8.14170	11.77880 } 14.48410 }		Second method		{ 69.12165* 69.12324
10.01188					
Chlorides of Potassium produced.	Silica for		Rough Relationship (see below).	Corrected Relationship Ag : KCl = 100.	
	100,000.	69,120.			
Chloroplatinate of Potash, 2nd Third, β 237	{ 2 to 2½ 2 to 2½ 2 to 2½	1.4 to 1.75 Average 1.57	69.11956 69.11989 69.12165	69.11799 m 69.11832 69.12008 M	
Chlorate of Potash, β 233 ..	5	3.5	69.12324	69.11974	
					Average 69.11903 Log. = 1.8395976

The estimations of 1860 gave, as the deduction made for silica, 69.1000.

XI. Relation between Silver and Chloride of Sodium, γ 19—28.

Chloride of Sodium.	Equivalent in Silver.		Ag : NaCl = 100.		Average.
	Saline Limit.	Silver Limit.	Saline Limit.	Silver Limit.	
6.07976	11.20817	11.22367	54.2440	54.16909	54.20654
5.73147	10.56710	10.57960	54.23881	54.17474	54.20677
11.33407	20.90819 } 11.23946 }		Second method		{ 54.20875 54.20527
6.09238					
Chlorides of Sodium produced.	Silica for		Rough Relationship.	Corrected Relationship. Ag : NaCl = 100.	
	100,000.	54,206.			
Chloroplatinate of Sodium, 1st Third, β 247	{ 3.5 3.5	1.90 1.90	54.20654 54.20677	54.20464 54.20487	
Carbonate, β 244	5	2.71	54.20875	54.20604 M	
Chloroplatinate, Last Third	4.5	2.44	54.20527	54.20283 m	
					Average 54.20460 Log. = 1.7340361

The estimations of 1860 and 1865 (α 280; β 286) gave, as the deduction made for silica, 54.204.

XII. Relation between Silver and Chloride of Ammonium, γ 20—30.

Chloride of Ammonium.	Equivalent in Silver.		Ag : NH ₄ Cl = 100.		
	Saline Limit.	Silver Limit.	Saline Limit.	Silver Limit.	Average.
5.56114	11.20298	11.22098	49.63983	49.56020	49.60001
5.57015	11.22115	11.23915	49.63974	49.56024	49.59999
5.42614	<div> <div>10.93999</div> <div>11.30335</div> <div>or 11.30349</div> <div>12.19487</div> </div>		<div> <div>Second method.. ..</div> <div>{</div> <div>49.59914</div> <div>49.60106* M</div> <div>or 49.60043</div> <div>49.59872* m</div> </div>		49.59914
5.60658					
6.04850					
			Average 49.59978 (66)		
			Log. = 1.6954798 (

The chloride in the last estimation was prepared by Deville.

The estimations of 1860 (α 289) gave 49.5944; those of 1865 (β 57), 49.5968.

XIII. Relation between Silver and Bromide of Potassium, β 303.

No. of Experiment.	Bromide of Potassium.	Equivalent in Silver.	Ag : KBr = 100.
4	10.3519	9.3816	110.3426
5	14.8803	13.4850 ?	110.3470* M
6	25.11427	22.7612*	110.3381
8	15.0454	13.6360	110.3359
9	21.6969	19.6629	110.3444
10	9.20526	8.34305	110.3345*
11	20.1233*	18.23665	110.3454*
13	11.0613	10.0253	110.3339 m
14	16.3032	14.77585	110.3368*
Average			110.3398*

The total number of experiments was fourteen; but Nos. 1, 2, 3, 7, and 12 might be considered as affected by errors. However, M. Stas showed little satisfaction at this series of experiments. Of all the samples of bromide of potassium that of No. 9 is the only one whose contents of silica has been estimated. This bromide gave a chloride with 8.5-100,000ths to 9-100,000ths of silica; which represents from 5.7 to 6.2 for 110,000 of bromide of potassium. The relation is therefore brought from 110.3444 to 110.3385, the figure which I have adopted in my calculations. M. Stas has collected and weighed the bromide of silver produced by this experiment, No. 9; the result being 21.7301

* Ann. Chim. Phys., 6th Series, vol. vii., April, 1886.

of bromide of potassium and 19.6929 of silver; gave 34.2817 of bromide of silver, from which we get—

$$\text{Ag} : \text{AgBr} = 100 : 174.0815,$$

which is identical with the mean of Table V., and also—

$$\text{KBr} : \text{AgBr} = 100 : 157.7614^*,$$

which combined with the relation of Table V. leads to—

$$\text{Ag} : \text{KBr} = 100 : 110.3445,$$

which is identical with the figure shown above.

In 1882 (γ 37) M. Stas stated that he had not succeeded in procuring the hydrate or carbonate of potassium in a state of purity, and that it was, therefore, impossible for him to fix this relationship more definitely.

XIV. Relation between Silver and Bromide of Sodium, γ 46.

Bromide of Sodium.	Equivalent in Silver.	Ag : NaBr = 100.
10.77950	11.29428	95.44211
14.85167	15.56152	95.43843 ^{*m}
13.97650	14.64387	95.44265 M
10.04296	10.52288	95.43927

Average 95.44062^{*}

The bromide used was obtained by saturating pure monosodic carbonate with the aid of hydrobromic acid. The chloride of sodium obtained from the same carbonate left, when volatilised, 5-100,000 of silica. Admitting that the retention of silica is proportional to the sodium contained in the two compounds, the bromide of sodium used in the experiment should contain 2.85 of silica per 100,000, or 2.72 per 95,441, which brings the relation to—

95.4379

$$\text{Log.} = 1.9797208$$

THE ACTION OF HYDROFLUORIC ACID ON SILICA AND SILICATES.

PRELIMINARY NOTICE.

By J. B. MACKINTOSH.

It has been known for some time that some silicates, such as zircon, are not affected by hydrofluoric acid, and this fact has been utilised in order to purify crude zircons for analysis,* and to separate the various constituent minerals in rocks.† Messrs. Fouqué and Lévy state—"L'acide fluorhydrique attaque d'abord les matières amorphes, puis les feldspaths, puis le quartz cristallisé, et enfin les silicates ferrugineux et le fer oxydulé. . . . Si, par exemple, on traite une ponce, mélange de matière amorphe et de minéraux cristallins, on attaque successivement la matière amorphe, les feldspaths, puis l'olivine, le fer oxydulé, l'amphibole, le pyroxène." My attention was first directed to this subject by finding that garnet was not affected in the slightest degree by the concentrated acid, and since then I have tried a larger number of silicates, about half of which are also unattacked. My results, however, differ somewhat from those of Fouqué and Lévy as quoted above. Generally speaking, those minerals which have a more condensed molecule are less easily attacked than those with a less condensed molecule, which fact is highly in favour of the "Natural System in Mineralogy" proposed by Dr. T. Sterry Hunt. When Dr. Hunt, to whom I am indebted for suggestions and information, first learned that I was experimenting in this direction, he predicted correctly the action on some species, and suggested that I should make my experiments quantitative.

The results of these quantitative experiments are of very great interest. I will, however, only give here the

difference between the two forms of silica, quartz, and opal. When 1 grm. of each, reduced to a uniform average size of $\frac{1}{100}$ cubic millimetre, was treated with an excess of dilute hydrofluoric acid (9 per cent) in the cold for one hour, the quartz lost only 1.56 per cent, while the opal had lost 77.28 per cent. With crystals of quartz and pieces of opal of corresponding size, the difference is still more strongly marked. Even when treated for one hour in concentrated (54 per cent) acid, quartz crystals suffered a diminution of weight of about 0.04 per cent and 0.24 per cent, while in the dilute acid for the same length of time opal lost 28.5 per cent. The differences in the amounts dissolved off different quartz crystals seems to have much more than merely chemical significance, and to be connected with those molecular dissimilarities which cause the differences between right- and left-handed quartz, the occurrence of plagihedral faces, and of those rhombohedral faces which differ in angle from the primitive form. —*School of Mines Quarterly*, vol. vii., p. 384.

ON THE CHEMICAL COMPOSITION OF HERDERITE AND BERYL,

WITH NOTE ON THE PRECIPITATION OF ALUMINUM AND SEPARATION OF BERYLLIUM AND ALUMINUM.*

By S. L. PENFIELD and D. N. HARPER.

(Concluded from p. 92).

4. On the Separation of Aluminum and Beryllium.

VARIOUS experiments convinced us that the following methods are not satisfactory: precipitation of the alumina as basic acetate, some beryllium being also precipitated; precipitation of the alumina with barium carbonate; solution of the beryllium in a boiling solution of ammonium chloride; by long boiling of a solution of ammonium chloride the solution becomes slightly acid, and according to our own experience some alumina is dissolved, while Genth† found that the beryllium was not completely dissolved. Solution of the beryllium in and precipitation of the alumina with ammonium carbonate gives unreliable results, and the method, when carried out as described by one of us in making a series of beryl analyses‡ gave too low results for beryllium.

We have made a large number of separations by dissolving the mixed chlorides in the least possible excess of caustic soda, diluting the solution largely, and precipitating the beryllium by boiling. This method has recently been proposed by Genth§ as the most reliable of the known methods, and Baker|| used it successfully in his analysis of beryl. Before using the method in our own work we made a series of experiments to determine its accuracy and to find out the best conditions for making the separation. A standard solution of beryllium chloride was made from purified K_2BeF_4 containing 0.1107 grm. BeO in every 50 c.c. Our standard solution of aluminum chloride contained 0.1002 grm. Al_2O_3 in every 50 c.c. Neither of the solutions contained any alkali and not more than traces of sulphuric acid.

The method was as follows:—50 c.c. of each solution were measured into a platinum dish and evaporated to dryness, the chlorides were dissolved in the least possible quantity of water, and a rather strong solution of pure soda, made from metallic sodium, was cautiously added until the precipitate which at first formed was completely dissolved. The contents of the dish were then rinsed with cold water into a beaker containing about 800 c.c. of boiling water and the contents of the beaker boiled for

* From the *American Journal of Science*, vol. xxxii., p. 107.

† *Proc. Amer. Phil. Society*, xxi., 694, 1884.

‡ *Loc. cit.*

§ *Loc. cit.*

|| *Amer. Chem. Journal*, vii., 175.

* Linnemann, *CHEMICAL NEWS*, November 6th, 1885.

† "Mineralogie Micrographique," F. Fouqué et Michel Lévy. Paris, 1879, p. 116.

one hour, replacing from time to time the water which evaporated. The beryllium separates out as a granular precipitate which is easy to filter and wash. After acidifying and concentrating the filtrate the alumina was precipitated with ammonia. Our experience has taught us that the best results are obtained by dissolving the dried chlorides in the least possible quantity of water and using as little soda as possible for dissolving the aluminum and beryllium.

Below we have given in tabulated form the results of our experiments.

	Weight of Al_2O_3	Weight of BeO.
	0.1041	0.1093
	0.1057	0.1080
		0.1096
	0.1045	0.1099
		0.1107
	0.1032	0.1093
	0.1037	0.1093
	0.1031	0.1083
Average	0.1040	0.1093
Standard	0.1002	0.1107

The precipitates were in all cases ignited for a long time to full redness over a ring burner. It will be seen that the BeO is quite constant and the average only a little below the standard. The Al_2O_3 is in all cases too high. If the quantity of mixed beryllium and aluminum oxides be determined in any compound, and then the BeO separated according to the above method and the Al_2O_3 determined by difference, the results will be very nearly correct. The determinations of Al_2O_3 and BeO in beryl given earlier in this article was made in this way.

To account for the excess of Al_2O_3 we thought that perhaps appreciable quantities of silica were dissolved from the glass by boiling the alkaline solutions of the mixed oxides for one hour. We therefore in every case dissolved the oxides in hydrochloric acid and deducted from their weight a slight quantity of insoluble matter amounting to about 0.0010 gm. in the Al_2O_3 and 0.0004 gm. in the BeO. The excess of Al_2O_3 must, therefore, have come from some other cause than silica dissolved from the glass. The alkaline solutions are so dilute that the glass is very little acted on, and determinations made in a platinum dish convinced us that the separation can be made just as well in beakers. We have concluded that the beryllium is not completely precipitated from a solution in soda by boiling and that it is not possible to wash out all of the soda from the precipitate. The following experiments on the determination of BeO in beryl will show this. The first column gives the weight of BeO obtained by boiling the soda solution, the second the same oxide dissolved in hydrochloric acid, re-precipitated with ammonia, and ignited.

0.1476	0.1440
0.1464	0.1422
0.1330	0.1300
0.4270	0.4162

The total BeO in these experiments weighed 0.4270 on first precipitation, 0.4162 on second, a loss of 0.0108. Calculating by proportion the loss which would result from 0.1107 gm. BeO, the quantity used in our first experiments, we find—

$$0.4270 : 0.1107 = 0.0108 : x. \quad x = 0.0027$$

that is, in the quantity of BeO which we used in making our experiments, the BeO was too heavy by about 0.0027 gm., representing probably some soda compound which could not be removed by washing. The excess in the Al_2O_3 is due to the BeO which was not precipitated by boiling. If we take the sum of the Al_2O_3 and BeO in the average of our determinations 0.2133 and deduct from it 0.0027, we have 0.2106 against 0.2109, the sum of Al_2O_3 and BeO in our standard. The following determinations

made from our standard solutions, the boiling of the soda solutions being done in platinum, confirm us in this. First weight of BeO 0.1087, after solution and re-precipitation 0.1068, weight of Al_2O_3 0.1041. $0.1068 + 0.1041 = 0.2109$, the weight of mixed oxides in our standard. We conclude, therefore, that the separation is not as perfect as our results would indicate. The error is, however, very constant, the amount of BeO which is not precipitated being almost exactly equal to the amount of soda which it seems impossible to remove from the precipitate by washing.

When phosphoric acid is present alumina may be separated from beryllium by boiling the solution of the mixed chlorides with barium hydroxide. The alumina goes readily into solution, while the precipitate containing the barium phosphate and beryllium is easy to filter and wash. After dissolving the precipitate and separating the barium with sulphuric acid, a beryllium phosphate can be precipitated with ammonia. After weighing this the P_2O_5 may be determined by means of ammonium molybdate and the BeO by difference, or the precipitate may be fused with sodium carbonate and the fusion soaked out with water, which gives almost a complete separation of phosphoric acid from beryllium. If phosphoric acid is also to be determined it must be borne in mind that very perceptible quantities of it will be found in the barium sulphate precipitate.

We have also observed that when Al_2O_3 is ignited over a ring burner till a constant weight is obtained, then over a blast lamp, there is a slight loss, amounting in the quantities which we have used in making the above experiments to about 0.0010 gm. What this loss represents we are not able to say. Usually in practical work this error can not be avoided, because it is necessary to dissolve the ignited Al_2O_3 to test for traces of SiO_2 or iron, and it is almost impossible to dissolve Al_2O_3 which has been strongly ignited over a blast lamp. The same is true for ignited BeO. After strong ignition over a ring burner there is still a loss of about 0.0013 in the quantities which we used, by igniting for five minutes over a blast lamp. This may be done, however, as the ignited BeO is readily soluble in hydrochloric acid.

In closing we wish to express our thanks to Messrs. Geo. J. Brush, L. Stadtmüller, and Geo. F. Kunz for the rare material which they kindly furnished for carrying out this investigation.

THE SANITARY VALUE OF THE CHEMICAL ANALYSIS OF POTABLE WATERS.*

By WILLIS G. TUCKER, PH.D.

FOR the past six months or more the subject of our city water supply has received an unusual amount of attention from the citizens of Albany. Very naturally questions concerning the various methods of water analysis and their value have come under discussion, and it is possible that a brief description of those processes which are employed by chemists to-day and a discussion of their respective merits may be of interest at this time. It may be profitable also to inquire what are the questions which a chemical analysis can positively answer and incidentally to consider the probabilities of disease transmission by water used for drinking and the effect of natural oxidation by aëration in purifying those which are polluted by sewage matter.

The general appearance and physical properties of a water will naturally first attract attention when its quality is questioned. An ideally pure water will be clear and colourless, odourless and tasteless, but these qualities, however desirable in themselves, do not necessarily indicate freedom from pollution. Waters which have penetrated through the soil are generally bright and clear

* A Paper read before the Albany Institute.

from the filtration they have undergone, and may have neither odour nor taste and yet be very dirty waters chemically, while surface waters may show a decided colour and even turbidity, may have an earthy, vegetable, or peaty odour and taste, and yet be quite free from harmful constituents. *Pure* water does not exist in nature, all dissolved or suspended substances being impurities in water as such, though by no means necessarily harmful. The sensible properties of a water, therefore, unless it be so foul that there is no mistaking its pollution, afford little information as to its quality. Water may percolate through the soil for a mile under a mountain and be as clear as crystal and yet carry typhoid fever from a hamlet on one side to dwellers on the other, as in the celebrated and well authenticated case at Lausen, Switzerland.

The suspended matter contained in potable waters, and naturally most abundant in surface waters, usually consists chiefly of clayey matter, easily removed by filtration on a large or small scale or by mere subsidence. In some cases, however, as in the James river water which supplies Richmond, the suspended matter is so finely divided that its removal is well nigh impossible, but such matter may generally be disregarded as unimportant from a hygienic point of view. The dissolved constituents consist both of gaseous and solid substances. The former may be the atmospheric gases only, and aside from the indications which the quantities of nitrogen and oxygen and the ratio between them are thought by some to afford as to the amounts of organic matter which are undergoing oxidation their quantity is of little importance. Sulphuretted hydrogen and other noxious gases may indeed be present as the result of putrefactive changes or peculiar conditions, and the recognition of such constituents may become a matter of importance, not because they are in themselves capable of producing disease in the quantities which may be present in water, but because their existence throws light upon the chemical changes which are taking place.

The dissolved solid constituents of potable waters are both inorganic and organic, the latter either of animal or vegetable origin. Up to twenty years ago the ordinary method of quantitative determination was to evaporate a definite quantity of the water to dryness in a platinum dish, weigh the residue, calculate the percentage of total solids, and then determine the organic or volatile matter by the loss resulting from the ignition of the total solid residue, due correction being made for the loss of carbonic acid. A complete analysis was then usually made of the mineral constituents, but as the precise amounts of these are of little importance and as the method described for determining the organic matter afforded no clue to its nature and was too inexact to be of value even in ascertaining the amount with accuracy, it may be readily seen that the results thus obtained were of little or no sanitary value. In speaking of the exact determination of the mineral constituents as unimportant reference was had to the lime, magnesia, iron, and other salts usually occurring in all natural waters save rain water, and not to the chlorine, phosphoric acid, nitrates, and nitrites which are important, but which formerly received less attention than at present. For manufacturing purposes of course a soft water is generally to be preferred. Hard waters, however, act upon lead less than soft ones, while on the other hand they occasion a waste of soap and are not desirable for culinary purposes; but these are incidental questions, and it cannot be said to be proven that the amount of mineral matter in potable water exercises much influence upon its healthfulness. In most cases a mere determination of the hardness is quite sufficient, a water not too hard being generally preferred, though the total solids are likewise determined when a complete analysis is made.

Let us now briefly consider those inorganic constituents which are generally regarded as important from a hygienic standpoint.

1. *Chlorine*.—This occurs chiefly in combination with sodium. In waters not naturally brackish the determination of its amount is regarded as decidedly important.

Chlorides occur in all human excreta and slop waters, and, therefore, in all sewage, and their presence in considerable quantity is a sign of probable contamination. The estimation is generally made volumetrically with a nitrate of silver solution. Over five parts in 100,000 were regarded by the Rivers Pollution Commission of Great Britain as in most cases due to sewage contamination.

2. *Phosphoric Acid*.—“Much nonsense,” says Wanklyn, “has been talked about phosphates.” This talk has had to do with the presence of phosphates in sewage and the evidence afforded by them of such contamination. The fact, however, is that in presence of carbonate of lime phosphates can only exist in exceedingly small traces in a clear water, but a qualitative test for their presence is usually made.

3. *Nitrites and Nitrates*.—These compounds are believed to result mainly from the oxidation of nitrogenous organic matter, chiefly animal, and are considered by some chemists as indicating quite accurately the amount of such defilement. In themselves, of course, they are harmless, but if they aid us in determining the amount of pollution their quantity becomes a matter of importance. It is now pretty generally conceded that the conversion of nitrogenous organic matter into these forms takes place under the influence of micro-organisms and is a process of fermentation, the rapidity of which depends upon degree of dilution, temperature, and other conditions. Recent experiments, as, for instance, those of Warrington at the Rothamsted laboratory reported in *Nature*, for October 30, 1884, seem to prove quite conclusively that such is the case, and if so, the old view that nitrification is a mere oxidation must be abandoned, and our ideas concerning the value of natural aëration, long considered by many chemists so important, must be greatly modified. Warrington asserts that nitrification will not take place in an acid solution. Some base must be present with which the nitric acid formed may combine, and when this is exhausted the oxidation ceases. If this is true then a study of the amount of certain mineral constituents present in a water which may furnish bases to the nitric acid produced, becomes indirectly important in determining the rapidity and completeness with which sewage matter may be oxidised, and a study of this subject, yet practically undeveloped, bids fair to yield valuable results.

At the same time it is to be borne in mind, as Wanklyn and others have pointed out, that certain mineral strata yield nitrates to water containing no organic matter, and that processes of vegetation in rivers and lakes withdraw them from water. Also that nitrates once formed may be again reduced to ammonia compounds or even to free nitrogen. If so, then an undue importance has been attached to the determination of nitrogen in this form, by Frankland and others, who make use of the term “previous sewage contamination” to denote the amount of sewage which has been discharged into a water and undergone oxidation, estimating the same by determining the total combined inorganic nitrogen present, as ammonia, nitrates, and nitrites, and after deducting the amount of nitrogen present in these forms in rain water, calculating how much “average London sewage” would be required to account for it. It will therefore be seen that much difference of opinion exists as to the degree of importance to be attached to the presence of these compounds in water, and that the questions involved are exceedingly intricate and as yet very far from being settled. Various methods are employed in their determination, none of which are perfectly satisfactory.

We may now dismiss from further consideration the inorganic constituents of potable waters, and proceed to describe those methods of analysis developed during late years which have for their object the determination of the amount and so far as possible the nature of the organic constituents, so much more important than the inorganic, from a sanitary point of view. The following are the most important of these processes:—

1. *Permanganate Methods*.—In 1849 Forchammer pro-

posed the use of permanganate of potassium for the determination of the oxidisable matter in water. This salt imparts, even in very small quantities, a decided pink colour to water, and as it contains a large amount of oxygen which it readily gives up to reducing bodies, thereby losing its characteristic colour, its use affords a ready method for the determination of the amount of many such substances in a state of solution. As applied to the determination of organic matter, however, the results can have no absolute value, since different kinds of organic matter require for oxidation different amounts of oxygen, and moreover differ in the completeness with which they are oxidised and the length of time required. Much also depends upon the exact method in which the test is applied, and various inorganic compounds which may be present reduce the permanganate and become a source of error. Nevertheless this test has a certain value, and it was at one time even thought that the amounts of putrescible matter might be estimated by the amount of permanganate decolourised during the first few minutes, since such matter probably first undergoes oxidation. Frankland held this view, as did Angus Smith, but the former has of late entertained a different opinion. W. A. Miller, Kubel, Tidy, Letheby, Schultze, and others have proposed particular methods for the application of this test, that most in use at the present time being Tidy's modification, which consists in the addition of a definite amount of permanganate solution to a certain quantity of the water acidified with sulphuric acid. At the end of a certain length of time the amount of permanganate remaining is determined, and the amount of oxygen consumed is calculated and reported as "oxygen absorbed." Very generally, two determinations are made on different samples of the water, the permanganate being allowed to act for fifteen minutes in one case and for three or four hours in the other.

Tidy and his adherents attach great importance to the results thus obtained. Frankland admits that they are not without value, and finds that they corresponded in 1418 out of 1686 cases quite closely with those obtained by his own very elaborate method presently to be described. Wanklyn condemns the method as misleading on account of want of delicacy, and the fact that albumen is not readily attacked by the standard solution of permanganate, while, as Frankland long ago pointed out, such bodies as starch and cane-sugar take up less than the one-hundredth part of the oxygen required for total oxidation. The majority of water analysts probably realise the imperfections of all permanganate methods, but consider their indications as not without a certain value. In this connection it may be remarked that Wanklyn has proposed and patented a method known as the "moist combustion process," in which an alkaline solution of permanganate is distilled with the water and the amount of permanganate consumed determined. It has not been received with much favour.

2. *Wanklyn and Chapman's Albumenoid-Ammonia Process.*—The ammonia method so well known and largely employed at the present time was brought forward by Wanklyn, Chapman, and Smith, in 1867. The modified process now in general use is described in the fifth edition of Wanklyn and Chapman's "Water Analysis." No method has ever found such general favour among analysts, a fact perhaps in part owing to the comparative ease with which the test is applied, the general nicety of the process, and the seeming accuracy—certainly delicacy—of the method. Nevertheless it has been harshly criticised by many, and especially by Frankland and his followers.

In this test a definite quantity of water is boiled in a retort, some carbonate of sodium having been added if necessary to render the water alkaline, and the ammonia which existed as such in the water or has resulted from the decomposition of urea and like substances, passes over with the escaping steam, which is condensed and the amount determined with Nessler's solution and reported

as "free ammonia." When this has all been given off an alkaline solution of permanganate of potassium is added, and the distillation continued. Certain kinds of organic matter containing nitrogen are thus decomposed, giving off a part or all of their nitrogen as ammonia, and since albumen is one of these, the ammonia so obtained is called "albumenoid-ammonia," and reported as such.

This process was the first to come into general use, which claimed to distinguish readily putrescible nitrogenous matter from those organic substances which are with greater difficulty converted into ammonia, and much importance was naturally attached to the results obtained in distinguishing pollution due to animal matter from that of vegetable origin, but as different amounts of ammonia are yielded by the same weights of different substances, and as the conversion of many such into ammonia is by no means complete, the results can have no absolute insignificance. On these and other grounds Frankland rejects this method utterly. Tidy, likewise, while admitting that the process might be used to discriminate between a water of excellent quality and one exceedingly bad, holds that when water of intermediate character is under examination, it "utterly and entirely fails." It is to be borne in mind, however, that both Frankland and Tidy are committed to methods of their own, which they advocate not without the exhibition of a partisan spirit, and their conclusions are, therefore, hardly entitled to the same weight as those of less prejudiced, though, perhaps, less distinguished, experts. The rank and file of water analysts have accepted this method as affording very valuable information, and in the elaborate "Preliminary Report on the Results of an Investigation made by direction of the National Board of Health, as to the Chemical Methods in Use for the Determination of Organic Matter in Potable Water," made by Professor Mallet, of the University of Virginia, in 1881, and printed in the report of the National Board of Health for 1882, the author, while he points out the defects of the process, finds "that it is admittedly simple and easily carried out;" that "the value of the results depends more upon watching the *progress* and *rate* of the evolution of the ammonia than upon determining the total amount:" and that "taking the results by this process as recorded, we find a great deal of similarity between the figures for albumenoid ammonia and those for organic nitrogen (by the combustion process), but with frequent discrepancies of varying extent such as prevent the one being taken as the accurate measure of the other."

3. *Frankland and Armstrong's Combustion Process.*—This is the third and last of the important processes now in use. It was brought forward by its originators in 1867, and first described in print in the *Journal of the Chemical Society* (London) for March, 1868, and is by far the most elaborate method of any in use. It was employed by the Rivers Pollution Commission of Great Britain in the examination of a large number of waters. The process consists in the evaporation of a stated quantity of the water which has been freed from all the carbon and nitrogen which existed in it in an inorganic form, excepting in ammonia, by treatment with a saturated solution of sulphurous acid, by which the nitrates and nitrites are reduced with the expulsion of their nitrogen, and the carbonates decomposed with liberation of their carbonic acid. Nitrogen in ammonia is fixed, and has to be deducted in the final computation. The residue obtained is then submitted to organic analysis, resulting in the conversion of the carbon into carbonic acid, and the liberation of the nitrogen as such. The mixture of gases is then subjected to volumetric gas-analysis, and the results finally reported as parts of "organic carbon" and "organic nitrogen" in 100,000 of water. The relative proportion of nitrogen to carbon is supposed to throw light upon the nature of the organic matter originally present, since in animal substances the ratio is higher than in vegetable. Frankland finds that the ratio of nitrogen to carbon is for upland surface waters, on an average,

1 to 10; for water from cultivated land, 1 to 6; for shallow wells, 1 to 4; for sewage, 1 to 2. It has been found, however, that the effect of oxidation upon peaty matter is to diminish the proportion of carbon, while during the oxidation of animal matter it is the nitrogen which diminishes most rapidly. Therefore, the proportions of nitrogen to carbon in vegetable and animal matter vary in opposite directions during oxidation, a fact which greatly adds to the difficulty of deciding as to the nature of the organic matter present.

This process is, in theory, the most scientific and accurate of any ever proposed, but it is exceedingly difficult, requiring costly and elaborate apparatus and especial skill on the part of the operator. Mallet says, "It is better adapted to regular use in the analysis of many samples of water in a large public laboratory, than to occasional use by a private individual in now and then examining a sample of water." For these reasons, chiefly, it has not come into general use, and in this country it has been employed by but very few chemists. Objections on the score of difficulty, however, should not be allowed to weigh against the process itself if it is of value, but on this point much difference of opinion exists. As might be supposed, Wanklyn and Tidy condemn it, and while most chemists admit that the principle is a good one, it is pretty generally believed that its indications are by no means as reliable as they are claimed to be by the originators of the process. Mallet, after summing up its errors and the objections to it, says:—"The combustion process, in its present form, cannot be considered as 'determining' the carbon and nitrogen of the organic matter of a water, in a sense to justify the claim of 'absolute' value for its results, which have been denied to those of all other methods. It is but a method of approximation involving sundry errors, and in part a balance of errors."

(To be continued.)

NOTICES OF BOOKS.

The Life and Labours of John Mercer, F.R.S., F.C.S., &c.,—the Self-taught Chemical Philosopher. By E. A. PARNELL, F.C.S. (Author of "Applied Chemistry"). London: Longmans, Green, and Co.

WE have here, at last, a memoir of a man of whom not only his native district, but the tinctorial chemistry of Britain, has every reason to be proud. Though reared amidst circumstances anything but favourable, and living at a time when manuals of chemistry were both scarce and imperfect, he mastered by his unaided exertions one of the most delicate and complicated departments of chemical art, and became a brilliant and successful inventor. Not only so: he gained a profound insight into the philosophy of chemistry, speculating acutely on such subjects as catalysis, the mutual relations of the atomic weights, the motive theory of heat and electricity, &c. Nay, the occurrence of mould in some shipments of printed calicoes led him not merely to devise a remedy, but to speculate on the part played in fermentation by "organised" bodies, or what we now call germs or microbia. Mr. Parnell remarks that if his environment and pursuits had been different he might have developed the microbe doctrine of disease which we have now learnt from Pasteur and Koch.

But we shall be mistaken if we suppose that his attention was confined to the laboratory. He was an energetic man of business, who had he been swayed by greed would have acquired great wealth. He was active in promoting the welfare, physical, sanitary, moral, and religious, of his neighbours and dependents, and was, in short, in every way a power for good in his district.

John Mercer, at the age of eighteen, was bound apprentice to the colour-shop of Messrs. Fort, of the Oakenshaw Print-Works, the same establishment in which he after-

wards became a partner, and where he made his world-famed inventions. Here he met with an unforeseen, though not uncommon, difficulty. A young man who shows industry and ability, especially if he attracts the favourable notice of his employer, is liable to the jealous dislike of foremen, managers, &c., who use every artifice to injure his character, and are too often successful, unless the employer is one of those exceptional characters who see with their own eyes.

In consequence of the notorious "Berlin decree" of the first Napoleon, Messrs. Fort were compelled to reduce their establishment, and, as they offered to cancel the indentures of all apprentices who were willing, Mercer took the opportunity and left their service, and returned to his original business of a hand-loom weaver, to which he added that of dyeing. He succeeded, we are told, in making profitable use of the imperfectly spent materials of the print-works, which he purchased at a low price. In the spring of 1814 occurred a little incident which had great influence on his industrial career. At an old book-stall in Blackburn he met with a copy of Parkinson's "Chemical Pocket-Book, or Memoranda Chemica." This work, he says, introduced him into a new world, and gave a definite direction to his experiments. In 1817 he succeeded in applying the orange antimony sulphide in calico-printing, an invention which brought him back to Messrs. Fort's works as the head of the colour-shop. Here he brought out a stream of successive inventions, several of which led to very popular styles. He detected the constitution of indigo-whites, and invented the application of chromate of potash in producing yellow and orange designs on variously coloured grounds, and of discharging indigo. His next step was the production of manganese bronze, with which he produced a number of telling styles. His method of extracting cochineal and lac by means of a neutral alkaline oxalate was another important advance, especially as cochineal was then very expensive.

In the colour-shop he adjusted the strengths of his solutions in a simple relation to the equivalents of the substances. In his receipts he divided the imperial gallon into 16 gills, and the gill into 16 spoons, each spoon being again divided into 16 parts. Mr. Parnell remarks that these gills were not the common gill; but he forgets that in Lancashire the gill has, from time immemorial, represented 10 fluid ounces, and not 5 as in the South of England.

About 1827 he devised a volumetric process for testing bleaching-powder and bichromate of potash. Next followed a new method of fixing Prussian blue, a new oxidising agent for catechu, the use of sulpho-cyanide of potassium as a discharge, and a new application of red prussiate as an oxidising agent. Two of his inventions "outside the factory" here deserve notice,—a process for making artificial magnetic iron oxide, and a method of bleaching palm oil. We find him next introducing the arseniates and phosphates as substitutes for cow-dung, making important improvements in "preparing" delaines, and employing aluminous lakes, dissolved in neutral ammonium oxalate, in steam styles. Then followed his assistant mordant liquor, his dry process for making stannate of soda. His studies on Turkey-red dyeing, on madder and garancine, on red and black liquors, on ferrocyanides and nitro-prussides, and on "the properties of alumina" are significant. It was his nature to trace to its cause, if possible, every phenomenon detected in the course of ordinary work, and to arrive at fresh results from the conclusions thus reached. To such a mind business and research ran hand in hand.

In 1848 the Oakenshaw firm was dissolved, and Mercer retired from business. His aim had always been the production of first-class work, and the reputation of the firm had been built upon such goods. But the morbid competition springing up in all industries "led to the large production of inferior goods at a cheaper rate,"—a kind of work out of harmony with his tastes. His most

striking discovery, though one which has not met with due practical appreciation, is the process of "mercerizing" cotton. It has been said in depreciation of this invention that the same effects can be produced more cheaply in the loom. This is simply nonsense; nothing done by or in the loom can increase the receptivity of cotton for colouring-matters. Mr. Parnell gives the true reason, namely, that "competition renders it expedient, in the judgment of the manufacturer, to sacrifice durability and intrinsic excellence" to shams and low prices. In a word mercerising did not agree with the "cheap and nasty" principle.

John Mercer ended his active and honourable career in his seventy-sixth year, 1866, after two years of severe suffering, regretted by all who had come within the sphere of his influence.

An Appendix contains a number of his laboratory notes and colour-shop receipts. Many of these have passed into general use, the more so as Mercer freely imparted to others knowledge which many would have kept a close secret. Others have lost their chief practical value now so many of the wares with which he worked have been superseded by the coal-tar colours. But we are of opinion that there is much here which will prove suggestive, whilst the whole of Mercer's career must prove a noble and encouraging example to the young industrialist.

Mr. Parnell deserves well of the chemical and technical world for this ably-compiled volume.

Barbados. Results obtained on the Experimental Field at Dodd's Reformatory. 1886.

WE have here a report presented by J. B. Harrison, Professor of Chemistry and Agricultural Science to the Colony, and J. R. Bovell, Superintendent of the Reformatory. These gentlemen have carried out a series of experiments on the growth of the sugar-cane, and have obtained some important results. The soil upon which they operated was decidedly poor, containing—nitrogen, 0.1018; phosphoric anhydride, 0.079; and potash, 0.106. The manure supplied contained nitrogen = ammonia, 56 lbs. per acre; soluble phosphate, 106.06 lbs.; reverted phosphate, 2.91 lbs.; and insoluble phosphate, 3.58 lbs. Potash was given at the rate of 34.83 lbs. per acre, the original intention being to use 56 lbs. per acre, but the potash salts purchased for this purpose were found to contain only 49.34 per cent of "muriate" instead of 80 per cent as represented.

The yield of canes was much greater when sulphate of ammonia was used as the source of nitrogen than in the case of nitrate of soda. The addition of potash salts along with the nitrogenous matters increased the weight of canes per acre by 4000 lbs. in case of sulphate of ammonia, and by 3000 lbs. in case of nitrate of soda. The results lead to the suspicion that potash exerts a special manurial action on the sugar-cane. It is to be noted that the amount of soluble ash (chiefly potash salts) is not appreciably increased by considerable doses of potash salts.

The influence of drought upon the composition of the sugar-cane is unfavourable. In two comparative cases it was found that the crystallisable sugar was reduced by drought 4 per cent, whilst the glucose was doubled and the woody fibre was increased from 12.50 to 14.72 per cent. By judicious manuring the yield of sugar was increased 11.4 per cent.

A number of experiments were made with various artificial cane-manures supplied by different merchants. This was "intended, if possible, to arouse some interest in these experiments among the planters,"—an object in which it entirely failed.

An unsatisfactory result of these investigations is that the cane does not contain the proportion of sugar in its juices with which it has been credited by different writers. The proportion of total sugars left in the megass is very much less than usually assumed.

"It has been common among chemists to calculate the proportion of sugar in the whole cane from the amount present in the juice extracted, assuming that that left in the megass possessed the same composition." Hence the total sugar in average canes will not exceed 16.5 per cent. Hence the extra amount of juice extracted by increased pressure is poorer in sugar, and contains at the same time more impurities than the juice expressed by lower pressures.

The Gas and Water Companies' Directory, 1886. Edited by CHARLES W. HASTINGS. London: Scientific Publishing Company (Limited).

THIS Directory, which has now reached its tenth yearly issue, shows the date of formation of each company, the date of its special acts, if any, the share capital, dividends, debts; the names of the chairman, manager, and secretary; the lessee, owner, or corporation; and, lastly, the population of the town, its distance from London, and the railways by which it is reached. There is no scientific or technical information, but the Directory will be exceedingly useful to all persons who have business with the companies in question.

Gas-Works Statistics, 1886. Edited by C. W. HASTINGS. London: The Scientific Publishing Company, Limited

THIS compilation shows in parallel columns opposite the name of each town the date when the returns given were made—one of which, we perceive, is as far back as June 30th, 1882—the tons of coal used, the annual make and sale of gas, the illuminating power, the price per cubic feet, the number of consumers, the price paid for public lamps, the average price obtained for coke, and the tons of sulphate of ammonia made. Under this last head the returns are few. We presume the fall in the value of all the by-products of the gas manufacture checks the extension of operations in this direction. The illuminating power has a very wide range, from 12 to 30 candles, the latter magnificent result being reached at Berwick-on-Tweed, at a figure which, though high, is decidedly below the price charged for a much inferior gas in many other places. The highest price per thousand cubic feet is 10s., and the lowest are at Hull 1s. 9d., and at Leeds 1s. 10d., with a discount of 2½ per cent. The prices stand in no definite relation to the illuminating power, nor yet, as far as we can perceive, to the prices of coal in the neighbourhoods.

A comparison of the respective quantities of gas made and sold in certain towns leads to some very curious results. Thus, in several cases, these two quantities are exactly equal, proving that leakage from the mains and other forms of waste have been reduced to zero. This speaks of careful management. In other towns, on the contrary, the sales fall short of the make by a serious proportion (such as 1-6th, or even 1-5th of the entire yearly production). This is to be regretted, as proving the existence certainly of waste, and possibly of a nuisance and a source of danger. But in one instance we note a still more interesting result. At Nelson-in-Marsden the annual make of gas is reported as 50,131, whilst the sales reach 54,888 thousands of cubic feet. We cannot help wondering of what the extra 4757 thousand cubic feet—in round numbers one-tenth of the yearly production—consisted of and how they were obtained.

In Scotland the illuminating power runs higher; the minimum is 25 candle power, 30 is a not unfrequent figure, whilst Maryhill heads the list with 48½, and this at the modest price of 3s. 3d. to 3s. 6d. Whether these results are due to superior skill in management or to the greater productiveness of Scotch coal we do not learn.

In Ireland the illuminating power is much the same as in England, the maximum being Larne, with 22 candle power, and the minimum Carlow, Killarney, and Newtownards, with 14.

The last section of the work is somewhat complicated, including Colonial, Continental, and American returns. The highest illuminating power, 30, is reached by the Fulton Company, of Brooklyn. Nine towns, chiefly in the United States, are supplied with "water-gas," two with naphtha-gas, and to one is appended the remark "naphtha and coal-steam gas." We can only hope that this is not the product obtained by passing steam over ignited coal, and which is so rich in carbon-monoxide that in case of escape poisoning is more to be feared than explosion.

The utility of Mr. Hastings' work is beyond all question.

Water-Works Statistics, 1886. Edited by C. W. HASTINGS.
London: The Scientific Publishing Company, Limited.

THIS annual work might—at least if the requisite information were procurable—be made a most valuable document for sanitarians and medical practitioners. The "source of supply" might in all cases, as it does in some, show the geological character of the drainage area, or of the ground in which the wells are sunk or the streams flow. We see with reference to some towns mention of "wells in the chalk," "wells in the sandstone," "greensand," "limestone," "springs in millstone grit," "inferior oolite," &c.

If other towns would give similarly explicit answers we have no doubt that the editor would gladly make use of the information supplied. At present these statistics throw but a very faint light on the quality of the water supplied, which both for sanitary and for trade purposes is a question of the first importance. Instead of the column headed "gravitation or pumping," which is a point of wonderfully little interest to the public, we should suggest that the hardness of the waters should be given, and by its side a column showing the death-rate of the district. We should thus be in possession of a very valuable mass of evidence showing the relative sanitary value of hard and soft waters.

Bulletin No. 4, Sugar Experiment Station, Kenner, Louisiana, and State Experiment Station, Baton Rouge, Louisiana. By W. C. STUBBS, Ph.D., Director. Issued by Thompson J. Bird, Commissioner of Agriculture.
Baton Rouge: Jastremski, State Printer.

THIS report does not, as might be inferred from a cursory glance at the title, refer to sugar growing, but treats of the cultivation of oats, especially in the southern portion of the United States. In those regions it has been hitherto kept in check by rust. Varieties have, however, been raised which are proof against this disease, and these Dr. Stubbs recommends for culture in Louisiana, using a dressing of 2 parts cotton-seed meal (of course after the removal of the oil) and 1 part superphosphate at the rate of 400 to 500 lbs. per acre. It appears that oats are the third cereal in importance in the United States, the yearly production amounting to 407,858,999 bushels.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 6, August 9, 1886.

Spectrum of the Negative Pole of Nitrogen. General Law of the Distribution of Rays in Band Spectra.—H. Deslandres.—(See p. 100).

Critical Temperatures and Pressures of Certain Vapours.—C. Vincent and J. Chappuis.—The author's results are given in the form of tables. The figures confirm their conclusions that the differences between the critical temperatures and the boiling-points are not constant for series of homologous bodies, but increase progressively. They enable us, further, to see that for isomeric bodies neither the critical temperatures nor the excess of such temperatures over the boiling-points are constant.

Variations of Solubility of Certain Chlorides in Water in Presence of Hydrochloric Acid.—Guillaume Jeannel.—From an examination of the author's numerical results it appears that for one and the same chloride the quantities of salt and of acid contained in a given volume of the solution may vary in considerable proportions without the sum of the equivalents changing by more than some thousandth parts. This sum is still the same, within some thousandths, whatever may be the chloride considered. Generally speaking the sum of the equivalents increases at first in proportion as the quantity of acid augments, attains a maximum, and diminishes slightly. The author proposes the following general law:—The solubility of chlorides which hydrochloric acid precipitates from the aqueous solution varies, in presence of this acid, in such a manner that the sum of the equivalents of water, of salt, and of acid forming the solution remains constant at the same temperature, whatever may be the chloride and whatever the proportions of the mixture.

Combinations of Ammonia with the Metallic Permanganates.—T. Klobb.—The author describes compounds of this class obtained by the direct addition of ammonia to silver, copper, cadmium, nickel, zinc, and magnesium permanganates. Cobaltous salts do not give a similar compound on account of the facility with which they are oxidised. The author has succeeded in preparing an ammoniacal cobaltic permanganate.

Chemical and Thermic Study of the Phenol-sulphuric Acids. Paraphenol-sulphuric Acid.—S. Allain-le-Canu.—Paraphenol-sulphuric acid forms colourless, hydrated, very deliquescent needles. The author has prepared its mono-potassium salt and its bromo-derivatives.

Presence of Lecithine in Plants.—E. Heckel and Fr. Schlagdenhauffen.—The authors have detected the presence of the decomposition products of lecithine in a number of vegetable preparations. These facts establish a new link between the animal and vegetable worlds. They confirm once more the great truth of the vital unity proclaimed by Claude Bernard, to which is now added the unity of evolution and of organic composition.

Brandy Free from Taste Manufactured from the Marc of White Wines.—Alph. Rommier.—Not suitable for abstraction.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xiv., No. 2, July 15, 1886.

On Sparteine and its Salts.—MM. Grandval and Valser.—The authors give the following new reaction:—In a watch-glass they place a drop of sulphuretted ammonium sulphide, and introduce a little sparteine or a particle of one of its salts. In an instant a permanent orange-red colouration appears. They have further examined the basic, neutral, and acid sparteine sulphates, as well as the hydriodate, hydrobromate, and hydrochlorate.

Constitution of Pylocarpine.—MM. Hardy and Calmels.—The authors give structural formulæ for pilocarpine, pilocarpidine, jaborine, and jaboric acid.

Vernine.—MM. Schulze and Boschard.—Vernine is a nitrogenous crystalline matter which may be extracted from *Vicia sativa*, *Pinus sylvestris*, &c. It is sparingly soluble in cold water, very soluble in boiling water, inso-

luble in alcohol. It dissolves readily in ammonia and in dilute nitric and hydrochloric acids. If a small quantity is evaporated with dilute nitric acid there remains a yellow spot, which if touched with ammonia passes to an intense red.

The Detection of Acid Magenta in Wines.—M. Sambuc.—A continuation of the author's controversy with M. Cazeneuve.

Physiological Effects of Kairine.—Morohovetz.—From the *Weekly Medical Review*.

Chemical Action of Bacterium Aceti.—Adrian Brown.—From the *CHEMICAL NEWS*.

Nature of Pepsine.—Karl Sundberg.—The author infers from his researches that pepsine is probably not of an albumenoid nature.

Importation of Nitrogen into France.—M. Suilliot.—The importations of nitrogen into France in its three principal forms—sodium nitrate, ammonium sulphate, and guano—represent a mean annual value of 28 million francs. Paris alone throws into the sewers nitrogen of the yearly value of 20 millions.

Determination of Calcium Nitrate contained in Crude Saltpetre.—P. Guyot.—Ten grms. of the sample are dissolved in distilled water, and a few drops of the alcoholic solution of phenol-phthaleine are added. The colourless mixture is heated to a boil and titrated with Decroizille's normal sodium carbonate, heating after every fresh addition of the alkaline salt. The rose colouration produced on adding the carbonate disappears when all the lime has passed into the state of calcium carbonate, the last drop giving a colouration which is stable at a boiling heat. It is then merely requisite to multiply the number of divisions corresponding to 5 grms. by the coefficient 1,673,517.5. The lime and the nitric acid are found separately by using the coefficients:—

Lime	571,445
Nitric acid	1,102,072.5

Calcium nitrate	1,673,517.5
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Resistance of Colchicine to Putrefaction.—J. Ogier.—Three dogs were poisoned with colchicine; one with 0.50 gm. administered hypodermically, another with 0.10 gm. administered in the same way, and the third with 0.50 gm. introduced into the stomach. All were exhumed after 5½ months, and examined. The first carcase was in a much better state of preservation than the second, and especially than the third, but in all the reactions of colchicine were distinctly obtained, though somewhat modified. Hence the author suggests that it is not colchicine which was extracted from the bodies, but a transformation-product presenting analogous reactions. Similar observations may apply to other alkaloids.

Production of Vanilline from the Resin of the Olive Tree.—A. Scheidel.—This resin yields vanilline if oxidised by permanganate in an alkaline solution. Before complete oxidation the mixture is oxidised with sulphuric acid, and the vanilline is extracted either with a current of steam or by agitation with ether.

Berichte der Deutschen Chemischen Gesellschaft zu Berlin.
Vol. xix., No. 4.

Condensation of Chloral Hydrate with Tertiary Aromatic Amines.—P. Boessneck.—In this second communication the author investigates the condensation of chloral hydrate with dimethylaniline, the synthesis of hexamethyl-paraleukaniline and the condensation of chloral hydrate with diethylaniline.

On Cholic Acid.—F. Mylius.—After prolonged researches, as here laid down, the author concludes that cholic acid contains, along with the carboxyl group, at least one hydroxyl, as appears from the formation of dyslisin, its last anhydride.

Chemical Association of Sulphuric Acid with Water, Judged according to the Changes of the Specific Gravity.—D. Mendeleeff.—This paper does not admit of reproduction without the three accompanying diagrams.

On Levulose.—A. Herzfeld and H. Winter.—Levulose as obtained by crystallisation from absolute alcohol has the composition $C_6H_{12}O_6$, and its watery solution deflects the polarised ray of light by $\alpha(D) = -71.4^\circ$.

Combinations of Perchlormethyl-mercaptan and Aniline or Toluidine.—B. Rathke.—With aniline the ultimate results of the reaction are triphenylguanidine, thiocarbanilide, and thioaniline. With toluidine the results are analogous.

Preparation of Methyl Violet by Means of Perchlormethyl-mercaptan.—B. Rathke.—Not adapted for useful abstraction.

Liberation of Heat as a Sign of the Association of Sulphuric Acid and Water.—D. Mendeleeff.—This paper requires the accompanying diagram and tables.

A Case of the Formation of Succinic-ethylester.—O. Davidoff.—The ester obtained by Prof. v. Richter is in fact a succinic ethylester. The melting-point of succinic acid as given in the text-books, viz., 180.5° , is incorrect; it should be 185° .

On Diparaxylyl-keton.—K. Elbs and G. Olberg.—The authors obtain this compound from paraxylol and phosgene in presence of aluminium chloride. It is a thick pale yellow liquid, boiling at 325° to 327° , and not congealing in the cold of winter. It is soluble in alcohol, ether, benzol, and petroleum ether. On reduction with zinc-powder and alcoholic potassa it yields diparaxylyl-carbinol.

A Correction.—M. Nencki and N. Sieber.—The authors find that previous to them Prof. Hüfner of Tübingen has isolated the crystals of reduced venous hæmoglobine.

Oxidation of Phthalic Alcohol.—E. v. Hjelt.—On heating orthoxylenyl chloride with water there is formed an oil, probably orthophthalic aldehyd, which gives with ammonia an intense blue compound. The colouring-matter dissolves in chloroform with a greenish-blue and in strong sulphuric acid with a violet-blue colour. It has no distinct absorption-spectrum.

Phthalide from Orthotoluylic Acid.—E. v. Hjelt.—The direct conversion of orthotoluylic acid has not hitherto been carried out. It may be very easily effected by the action of bromine at 140° .

Meta-nitro-cumenyl-acrylic Acid and its Derivatives—Oskar Widman.—We have here an account of the salts of this acid, of meta-amido-cumenyl-acrylic acid, of meta-acetamido-cumenyl-acrylic acid, diacetamido-cumenyl-acrylic acid, meta-oxycumenyl-acrylic acid, meta-nitro-cumenyl-acrylic acid dibromide, meta-amido-cumenyl-propionic acid, and meta-acetamido-cumenyl-propionic acid.

Appendix to Memoir on Drying Apparatus.—Victor Meyer.—(See *Berichte*, xviii., p. 2999.) The liquids used for heating must be perfectly pure. The porcelain insets have been found unnecessary and even disturbing.

On a Base Isomeric with Benzidine formed on passing Aniline Vapour through Ignited Tubes.—A. Bernthsen.—The thick oil obtained as one of the products yields, on fractionate distillation with superheated steam, a base externally similar to benzidine and having the same percentage composition, though differing in its reactions. With potassium ferricyanide, unlike benzidine, it yields no reaction. Weak chlorine water gives a brown precipitate, whilst with benzidine it yields a splendid blue solution, turning first greenish blue and then red. Hence the author gives to the new base the name of iso-

benzidine. Bernthsen has further examined the mother-liquor remaining after the separation of isobenzidine.

On the Crystalline Forms of certain Derivatives of Acridine.—A. Bernthsen.—This paper is useless without the accompanying diagrams.

On Succinylsuccinic Ether.—A. Baeyer.—The author gives an account of paradioxy-terephthalic ether, of paradiamido-terephthalic ether, and of the reproduction of succinylsuccinic ether from dioxy-terephthalic ether.

On Malto-dextrine; a Reply to H. A. Herzfeld.—H. T. Brown.—A question of priority.

On Orthophenyl-diacrylic Acid.—W. H. Perkin, jun.—A brief notice of observations which will be published in detail in the *Journal of the Chemical Society*.

Attempts at the Synthesis of Coniine.—A. Ladenberg.—The author has obtained a base which is very probably identical with coniine.

Eurhodines: A new Class of Colouring-Matters.—O. N. Witt.—This interesting memoir does not admit of useful abridgment.

Carbamin-cyamides.—A. Wunderlich.—Poensgen's amidodicynic acid behaves in all respects like a cyanamide, in which an atom of hydrogen is replaced by the group CONH_2 .

On Actions of Contact.—D. Mendeleeff.—Not susceptible of abstraction.

Revue Universelle des Mines, de la Metallurgie, &c.,
Vol. xix., No. 3, May and June, 1886.

This issue contains no chemical matter.

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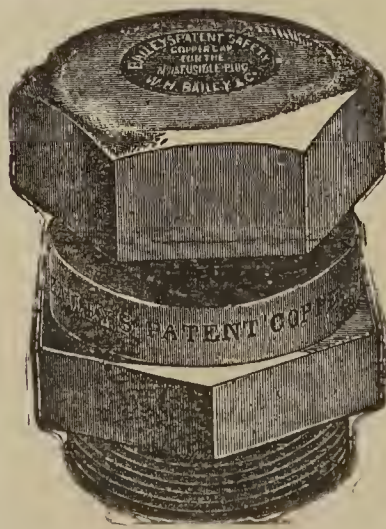
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THE CHEMICAL NEWS.

VOL. LIV. No. 1397.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BIRMINGHAM MEETING, SEPTEMBER 1, 1886.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR J. WILLIAM DAWSON, C.M.G., M.A., LL.D., F.R.S.,
F.G.S., Principal and Vice-Chancellor of McGill
University, Montreal, Canada.*

TWENTY-ONE years have passed away since the last meeting of the British Association in this great central city of England. At the third Birmingham meeting—that of 1865—I had the pleasure of being present, and had the honour of being one of the Vice-Presidents of Section C. At that meeting my friend John Phillips, one of the founders of the Association, occupied the Presidential chair, and I cannot better introduce what I have to say this evening than by the eloquent words in which he then addressed you:—"Assembled for the third time in this busy centre of industrious England, amid the roar of engines and clang of hammers, where the strongest powers of nature are trained to work in the fairy chains of art, how softly and fittingly falls upon the ear the accent of science, the friend of that art, and the guide of that industry! Here where Priestley analysed the air, and Watt obtained the mastery over steam, it well becomes the students of nature to gather round the standard which they carried so far into the fields of knowledge. And when on other occasions we meet in quiet colleges and academic halls, how gladly welcome is the union of fresh discoveries and new inventions with the solid and venerable truths which are there treasured and taught. Long may such union last; the fair alliance of cultivated thought and practical skill; for by it labour is dignified and science fertilised, and the condition of human society exalted." These were the words of a man who, while earnest in the pursuit of science, was full of broad and kindly sympathy for his fellow-men, and of hopeful confidence in the future. We have but to turn to the twenty Reports of this Association, issued since 1865, to see the realisation of that union of science and art to which he so confidently looked forward, and to appreciate the stupendous results which it has achieved. In one department alone—that to which my predecessor in this chair so eloquently adverted in Aberdeen, the department of education in science—how much has been accomplished since 1865. Phillips himself lived to see a great revolution in this respect at Oxford. But no one in 1865 could have anticipated that immense development of local schools of science of which your own Mason College and your admirable technical, industrial, and art schools are eminent examples. Based on the general education given by the new system of Board schools, with which the name of the late W. E. Forster will ever be honourably connected, and extending its influence upward to special training and to the highest university examinations, this new scientific culture is opening paths of honourable ambition to the men and women of England scarcely dreamed of in 1865. I sympathise with the earnest appeal of Sir Lyon Playfair, in his Aberdeen address, in favour of scientific education; but visiting England at rare intervals, I am naturally more impressed with the progress that has been made than

with the vexatious delays which have occurred, and am perhaps better able to appreciate the vast strides that have been taken in the direction of that complete and all-pervading culture in science which he has so ably advocated.

No one could have anticipated twenty years ago that a Birmingham manufacturer, in whose youthful days there were no schools of science for the people, was about to endow a college, not only worthy of this great city, but one of its brightest ornaments.* Nor could anyone have foreseen the great development of local scientific societies, like your Midland Institute and Philosophical Society, which are now flourishing in every large town and in many of those of less magnitude. The period of twenty-one years that has elapsed since the last Birmingham meeting has also been an era of public museums and laboratories for the teaching of science, from the magnificent national institutions at South Kensington and those of the great universities and their colleges down to those of the schools and field clubs in country towns. It has besides been an era of gigantic progress in original work and in publication—a progress so rapid that workers in every branch of study have been reluctantly obliged to narrow in more and more their range of reading and of effort to keep abreast of the advance in their several departments. Lastly these twenty-one years have been characterised as the "coming of age" of that great system of philosophy with which the names of three Englishmen, Darwin, Spencer, and Wallace, are associated as its founders. Whatever opinions one may entertain as to the sufficiency and finality of this philosophy there can be no question as to its influence on scientific thought. On the one hand it is inaccurate to compare it with so entirely different things as the discovery of the chemical elements and of the law of gravitation; on the other, it is scarcely fair to characterise it as a mere "confused development" of the mind of the age. It is indeed a new attempt of science in its maturer years to grapple with those mysterious questions of origins which occupied it in the days of its infancy, and it is to be hoped that it may not, like the Titans of ancient fable, be hurled back from heaven, or like the first mother find the knowledge to which it aspires a bitter thing. In any case we should fully understand the responsibility which we incur when in these times of full grown science we venture to deal with the great problem of origins, and should be prepared to find that in this field the new philosophy, like those which have preceded it, may meet with very imperfect success. The agitation of these subjects has already brought science into close relations, sometimes friendly, sometimes hostile, it is to be hoped in the end helpful, with those great and awful questions of the ultimate destiny of humanity, and its relations to its Creator, which must always be nearer to the human heart than any of the achievements of science on its own ground. In entering on such questions we should proceed with caution and reverence, feeling that we are on holy ground, and that though, like Moses of old, we may be armed with all the learning of our time, we are in the presence of that which while it burns is not consumed; of a mystery which neither observation, experiment, nor induction can ever fully solve.

In a recent address the late President of the Royal Society called attention to the fact that within the lifetime of the older men of science of the present day, the greater part of the vast body of knowledge included in the modern sciences of physics, chemistry, biology, and geology, has been accumulated, and the most important advances made in its application to such common and familiar things as the railway, ocean navigation, the electric telegraph, electric lighting, the telephone, the germ theory of disease, the use of anæsthetics, the processes of metallurgy, and the dyeing of fabrics. Even

* It was in 1865 that Sir Josiah Mason was, quietly and without any public note, beginning to lay the foundation of his orphanage at Erdington.

since the last meeting in this city, much of this great work has been done, and has led to general results of the most marvellous kind. What at that time could have appeared more chimerical than the opening up by the enterprise of one British colony of a shorter road to the East by way of the extreme west, realising what was happily called by Milton and Cheadle "the new North-west passage," making Japan the next neighbour of Canada on the west, and offering to Britain a new way to her Eastern possessions; or than the possibility of this Association holding a successful meeting on the other side of the Atlantic? To have ventured to predict such things in 1865 would have appeared quite visionary, yet we are now invited to meet in Australia, and may proceed thither by the Canadian Pacific Railway and its new lines of steamers, returning by the Suez Canal.* To-day this is quite as feasible as the Canadian visit would have been in 1865. It is science that has thus brought the once widely separated parts of the world nearer to each other, and is breaking down those geographical barriers which have separated the different portions of our widely extended British race. Its work in this is not yet complete. Its goal to-day is its starting point to-morrow. It is as far as at any previous time from seeing the limit of its conquests, and every victory gained is but the opening of the way for a farther advance.

By its visit to Canada the British Association has asserted its imperial character, and has consolidated the scientific interests of Her Majesty's dominions, in advance of that great gathering of the industrial products of all parts of the empire now on exhibition in London, and in advance of any political plans of Imperial federation.† There has even been a project before us for an international scientific convention, in which the great English republic of America shall take part, a project the realisation of which was to some extent anticipated in the fusion of the members of the British and American Associations at Montreal and Philadelphia in 1884. As a Canadian, as a past President of the American Association, and now honoured with the Presidency of this Association, I may be held to represent in my own person this scientific union of the British Islands, of the various Colonies and of the great Republic, which, whatever the difficulties attending its formal accomplishment at present, is certain to lead to an actual and real union for scientific work. In furtherance of this I am glad to see here to-day influential representatives of most of the British Colonies, of India, and of the United States. We welcome here also delegates from other countries, and though the barrier of language may at present prevent a larger union, we may entertain the hope that Britain, America, India, and the Colonies, working together in the interest of science, may ultimately render our English tongue the most general vehicle of scientific thought and discovery, a consummation of which I think there are, at present, many indications.

But, while science marches on from victory to victory, its path is marked by the resting places of those who have fought its battles and assured its advance. In looking back to 1865 there rise before me the once familiar countenances of Phillips, Murchison, Lyell, Forbes, Jeffreys, Jukes, Rolleston, Miller, Spottiswoode, Fairbairn, Gassiot, Carpenter, and a host of others, present in full vigour at that meeting, but no more with us. These were veterans of science; but, alas! many then young and rising in fame are also numbered with the dead. It may be that before another Birmingham meeting many of us, the older members now, will also have passed away. But these men have left behind them ineffaceable monuments

of their work, in which they still survive, and we rejoice to believe that, though dead to us, they live in that company of the great and good of all ages who have entered into that unseen universe where all that is high and holy and beautiful must go on accumulating till the time of the restitution of all things. Let us follow their example and carry on their work, as God may give us power and opportunity, gathering in precious stores of knowledge and of thought, in the belief that all truth is immortal, and must go on for ever bestowing blessings on mankind. Thus will the memory of the mighty dead remain to us as a power which—

Like a star
Beacons from the abode where the eternal are.

I do not wish, however, to occupy your time longer with general or personal matters, but rather to take the opportunity afforded by this address to invite your attention to some topics of scientific interest. In attempting to do this I must have before me the warning conveyed by Professor Huxley, in the address to which I have already referred, that in our time science, like Tarpeia, may be crushed with the weight of the rewards bestowed on her. In other words, it is impossible for any man to keep pace with the progress of more than one limited branch of science, and it is equally impossible to find an audience of scientific men of whom anything more than a mere fraction can be expected to take an interest in any one subject. There is, however, some consolation in the knowledge that a speaker who is sufficiently simple for those who are advanced specialists in other departments, will of necessity be also sufficiently simple to be understood by the general public who are specialists in nothing. On this principle a geologist of the old school, accustomed to a great variety of work, may hope so to scatter his fire as to reach the greater part of the audience. In endeavouring to secure this end I have sought inspiration from that ocean which connects rather than separates Britain and America, and may almost be said to be an English Sea—the North Atlantic. The geological history of this depression of the earth's crust, and its relation to the continental masses which limit it, may furnish a theme at once generally intelligible and connected with great questions as to the structure and history of the earth, which have excited the attention alike of physicists, geologists, biologists, geographers, and ethnologists. Should I, in treating of these questions, appear to be somewhat abrupt and dogmatic, and to indicate rather than state the evidence of the general views announced, I trust you will kindly attribute this to the exigencies of a short address.

If we imagine an observer contemplating the earth from a convenient distance in space, and scrutinising its features as it rolls before him, we may suppose him to be struck with the fact that eleven-sixteenths of its surface are covered with water, and that the land is so unequally distributed that from one point of view he would see a hemisphere almost exclusively oceanic, while nearly the whole of the dry land is gathered in the opposite hemisphere. He might observe that the great oceanic area of the Pacific and Antarctic Oceans is dotted with islands—like a shallow pool with stones rising above its surface—as if its general depth were small in comparison with its area. He might also notice that a mass or belt of land surrounds each pole, and that the northern ring sends off to the southward three vast tongues of land and of mountain chains, terminating respectively in South America, South Africa, and Australia, towards which feebler and insular processes are given off by the Antarctic continental mass. This, as some geographers have observed,* gives a rudely three-ribbed aspect to the earth, though two of the three ribs are crowded together and form the Europ-asian mass or double continent, while the third is isolated in the single continent of America.

* It is expected that on the completion of the connections of the Canadian Pacific Railway, the time from ocean to ocean may be reduced to 116 hours, and from London to Hong Kong to twenty-seven days.

† I should note here, in connection with this, the valuable volume of "Canadian Economics," edited by Mr. D. A. P. Watt, which was one of the results of the Montreal meeting.

* Dana, "Manual of Geology," introductory part. Green, "Vestiges of a Molten Globe," has summed up these facts.

He might also observe that the northern girdle is cut across, so that the Atlantic opens by a wide space into the Arctic Sea, while the Pacific is contracted toward the north, but confluent with the Antarctic Ocean. The Atlantic is also relatively deeper and less cumbered with islands than the Pacific, which has the higher ridges near its shores, constituting what some visitors to the Pacific coast of America have not inaptly called the "back of the world," while the wider slopes face the narrower ocean, into which for this reason the greater part of the drainage of the land is poured.* The Pacific and Atlantic, though both depressions or flattenings of the earth, are, as we shall find, different in age, character, and conditions; and the Atlantic, though the smaller, is the older, and from the geological point of view, in some respects, the more important of the two.

If our imaginary observer had the means of knowing anything of the rock formations of the continents, he would notice that those bounding the North Atlantic are in general of great age, some belonging to the Laurentian system. On the other hand, he would see that many of the mountain ranges along the Pacific are comparatively new, and that modern igneous action occurs in connection with them. Thus he might be led to believe that the Atlantic, though comparatively narrow, is an older feature of the earth's surface, while the Pacific belongs to more modern times. But he would note in connection with this that the oldest rocks of the great continental masses are mostly toward their northern ends, and that the borders of the northern ring of land and certain ridges extending southwards from it constitute the most ancient and permanent elevations of the earth's crust, though now greatly surpassed by mountains of more recent age nearer the equator. Before leaving this general survey we may make one further remark. An observer looking at the earth from without would notice that the margins of the Atlantic and the main lines of direction of its mountain chains are north-east and south-west, and north-west and south-east, as if some early causes had determined the occurrence of elevations along great circles of the earth's surface tangent to the polar circles.

We are invited by the preceding general glance at the surface of the earth to ask certain questions respecting the Atlantic. (1) What has at first determined its position and form? (2) What changes has it experienced in the lapse of geological time? (3) What relations have these changes borne to the development of life on the land and in the water? (4) What is its probable future?

Before attempting to answer these questions, which I shall not take up formally in succession, but rather in connection with each other, it is necessary to state as briefly as possible certain general conclusions respecting the interior of the earth. It is popularly supposed that we know nothing of this beyond a superficial crust perhaps averaging 50,000 to 100,000 feet in thickness. It is true we have no means of exploration in the earth's interior, but the conjoint labours of physicists and geologists have now proceeded sufficiently far to throw much inferential light on the subject, and to enable us to make some general affirmations with certainty; and these it is the more necessary to state distinctly, since they are often treated as mere subjects of speculation and fruitless discussion.

(1) Since the dawn of geological science it has been evident that the crust on which we live must be supported on a plastic or partially liquid mass of heated rock, approximately uniform in quality under the whole of its area. This is a legitimate conclusion from the wide distribution of volcanic phenomena, and from the fact that the ejections of volcanoes, while locally of various kinds, are similar in every part of the world. It led to the old idea of a fluid interior of the earth, but this is now generally

abandoned, and this interior heated and plastic layer is regarded as merely an under-crust.

(2) We have reason to believe, as the result of astronomical investigations,* that, notwithstanding the plasticity or liquidity of the under-crust, the mass of the earth—its nucleus as we may call it—is practically solid and of great density and hardness. Thus we have the apparent paradox of a solid yet fluid earth; solid in its astronomical relations, liquid or plastic for the purposes of volcanic action and superficial movements.†

(3) The plastic sub-crust is not in a state of dry igneous fusion, but in that condition of aqueo-igneous or hydro-thermic fusion which arises from the action of heat on moist substances, and which may either be regarded as a fusion or as a species of solution at a very high temperature. This we learn from the phenomena of volcanic action, and from the composition of the volcanic and plutonic rocks, as well as from such chemical experiments as those of Daubrée, and of Tilden and Shenstone.‡

(4) The interior sub-crust is not perfectly homogeneous, but may be roughly divided into two layers or magmas, as they have been called: an upper, highly siliceous or acidic, of low specific gravity and light-coloured, and corresponding to such kinds of plutonic and volcanic rocks as granite and trachyte; and a lower, less siliceous or more basic, more dense, and more highly charged with iron, and corresponding to such igneous rocks as the dolerites, basalts, and kindred lavas. It is interesting here to note that this conclusion, elaborated by Durocher and von Waltershausen, and usually connected with their names, appears to have been first announced by John Phillips, in his "Geological Manual," and as a mere common sense deduction from the observed phenomena of volcanic action and the probable results of the gradual cooling of the earth.§ It receives striking confirmation from the observed succession of acidic and basic volcanic rocks of all geological periods and in all localities. It would even seem, from recent spectroscopic investigations of Lockyer, that there is evidence of a similar succession of magmas in the heavenly bodies, and the discovery by Nordenskiöld of native iron in Greenland basalts affords a probability that the inner magma is in part metallic.||

(5) Where rents or fissures form in the upper crust, the material of the lower crust is forced upward by the pressure of the less supported portions of the former, giving rise to volcanic phenomena either of an explosive or quiet character, as may be determined by contact with

* Hopkins, Mallet, Sir William Thomson, and Prof. G. H. Darwin maintain the solidity and rigidity of the earth on astronomical grounds; but different conclusions have been reached by Hennessey, Delaunay, and Airy. In America Barnard and Crosby, Dutton, Le Conte, and Wadsworth have discussed these questions.

† An objection has been taken to the effect that the supposed ellipsoidal form of the equator is inconsistent with a plastic sub-crust. But this ellipsoidal form is not absolutely certain, or, if it exists, is very minute. Bonney has in a recent lecture suggested the important consideration that a mass may be slowly mobile under long-continued pressure while yet rigid with reference to more sudden movements.

‡ *Phil. Trans.*, 1884. Also Crosby in *Proc. Boston Soc. Nat. Hist.*, 1883.

§ Phillips says ("Manual of Geology," 1855, 493):—"If we regard them (the internal crystalline rocks) as acquiring solidification by cooling in zones parallel to the surface, we should have sheets of granitic and basaltic rocks generated below, the first uppermost, the last undermost, while above the several strata were produced in a series beginning at the bottom. In this sense the rocks of fusion may be called, with Lyell, *hypogene*. Certainly under particular areas of country are found evidence of the liquefaction of one set of igneous products after the solidification of others. Many dykes of basalt traversing granite show themselves to have been in fusion after the solidification of the granite." In various forms Phillips returns to this idea, as at pp. 556 and 564, in that unpretending manner which was his wont. Dr. Sterry Hunt has kindly directed my attention to the fact of Phillips's right of priority in this matter. Durocher in 1857 elaborated the theory of magmas in the *Annales des Mines*, and we are indebted to Dutton, of the United States Geological Survey, for its detailed application to the remarkable volcanic outflows of Western America.

|| These basalts occur at Ovisak, Greenland. Andrews has found small particles of iron in British basalts. Prestwich and Judd have referred to the bearing on general geology of these facts, and of Lockyer's suggestions.

* Mr. Mellard Reade, in two Presidential addresses before the Geological Society of Liverpool, has well illustrated this point and its geological consequence.

water. The underlying material may also be carried to the surface by the agency of heated water, producing those quiet discharges which Hunt has named crenitic. It is to be observed here that explosive volcanic phenomena, and the formation of cones, are, as Prestwich has well remarked, characteristic of an old and thickened crust; quiet ejection from fissures and hydro-thermal action may have been more common in earlier periods and with a thinner over crust.

(6) The contraction of the earth's interior by cooling and by the emission of material from below the over-crust, has caused this crust to press downward, and therefore laterally, and so to effect great bends, folds, and plications; and these modified subsequently by surface denudation constitute mountain chains and continental plateaus. As Hall long ago pointed out,* such lines of folding have been produced more especially where thick sediments had been laid down on the sea bottom. Thus we have here another apparent paradox, namely, that the elevations of the earth's crust occur in the places where the greatest burden of detritus has been laid down upon it, and where consequently the crust has been softened and depressed. We must beware, in this connection, of exaggerated notions of the extent of contraction and of crumpling required to form mountains. Bonney has well shown, in lectures delivered at the London Institution, that an amount of contraction, almost inappreciable in comparison with the diameter of the earth, would be sufficient; and that as the greatest mountain chains are less than 1-600th of the earth's radius in height, they would on an artificial globe a foot in diameter be no more important than the slight inequalities that might result from the paper gores overlapping each other at the edges.

(7) The crushing and sliding of the over-crust implied in these movements raise some serious questions of a physical character. One of these relates to the rapidity or slowness of such movements, and the consequent degree of intensity of the heat developed, as a possible cause of metamorphism of rocks. Another has reference to the possibility of changes in the equilibrium of the earth itself as resulting from local collapse and ridging. These questions in connection with the present dissociation of the axis of rotation from the magnetic poles, and with changes of climate, have attracted some attention,† and probably deserve further consideration on the part of physicists. In so far as geological evidence is concerned, it would seem that the general association of crumpling with metamorphism indicates a certain rapidity in the process of mountain-making, and consequent development of heat, and the arrangement of the older rocks around the Arctic basin forbids us from assuming any extensive movement of the axis of rotation, though it does not exclude changes to a limited extent. I hope that Professor Darwin will discuss these points in his Address to the Physical Section.

I wish to formulate these principles as distinctly as possible, and as the result of all the long series of observations, calculations, and discussions since the time of Werner and Hutton, and in which a vast number of able physicists and naturalists have borne a part, because they may be considered as certain deductions from our actual knowledge, and because they lie at the foundation of a rational physical geology.

We may popularise these deductions by comparing the earth to a drupe or stone-fruit, such as a plum or peach, somewhat dried up. It has a large and intensely hard stone and kernel, a thin pulp made up of two layers, an inner more dense and dark-coloured, and an outer less dense and lighter-coloured. These constitute the under-crust. On the outside it has a thin membrane or over-

crust. In the process of drying it has slightly shrunk, so as to produce ridges and hollows of the outer crust, and this outer crust has cracked in some places, allowing portions of the pulp to ooze out—in some of these its lower dark substance, in others its upper and lighter material. The analogy extends no farther, for there is nothing in our withered fruit to represent the oceans occupying the lower parts of the surface or the deposits which they have laid down.

Keeping in view these general conclusions, let us now turn to their bearing on the origin and history of the North Atlantic.

Though the Atlantic is a deep ocean, its basin does not constitute so much a depression of the crust of the earth as a flattening of it, and this, as recent soundings have shown, with a slight ridge or elevation along its middle and banks or terraces fringing the edges, so that its form is not so much that of a basin as that of a shallow plate with its middle a little raised. Its true permanent margins are composed of portions of the over-crust folded, ridged up, and crushed, as if by lateral pressure emanating from the sea itself. We cannot, for example, look at a geological map of America without perceiving that the Appalachian ridges, which intervene between the Atlantic and the St. Lawrence valley, have been driven bodily back by a force acting from the east, and that they have resisted this pressure only where, as in the Gulf of St. Lawrence and the Catskill region of New York, they have been protected by outlying masses of very old rocks, as, for example, by that of the island of Newfoundland and that of the Adirondack Mountains. The admirable work begun by my friend and fellow-student, Professor James Nichol, followed up by Hicks, Lapworth, and others, and now, after long controversy, fully confirmed by the recent observations of the geological survey of Scotland, has shown the most intense action of the same kind on the east side of the ocean in the Scottish highlands; and the more widely distributed Eozoic rocks of Scandinavia may be appealed to in further evidence of this.*

If we now inquire as to the cause of the Atlantic depression, we must go back to a time when the areas occupied by the Atlantic and its bounding coasts were parts of a shoreless sea in which the earliest gneisses or stratified granites of the Laurentian age were being laid down in vastly extended beds. These ancient crystalline rocks have been the subject of much discussion and controversy, and as they constitute the lowest and probably the firmest part of the Atlantic sea-bed, it is necessary to inquire as to their origin and history. Dr. Bonney, the late President of the Geological Society, in his Anniversary address, and Dr. Sterry Hunt, in an elaborate paper communicated to the Royal Society of Canada, have ably summed up the hypotheses as to the origin of the oldest Laurentian beds. At the basis of these hypotheses lies the admission that the immensely thick beds of orthoclase gneiss, which are the oldest stratified rocks known to us, are substantially the same in composition with the upper or siliceous magma or layer of the under-crust. They are, in short, its materials either in their primitive condition or merely rearranged. One theory considers them as original products of cooling, owing their lamination merely to the successive stages of the process. Another view refers them to the waste and rearrangement of the materials of a previously massive granite. Still another holds that all our granites really arise from the fusion of old gneisses of originally aqueous origin, while a fourth refers the gneisses themselves to molecular changes effected in granite by pressure. These several views, in so far as they relate to the oldest or fundamental Laurentian gneiss, may be arranged under the following heads:—(1) *Endoplutonic*, or that which regards all the old gneisses as molten rocks cooled from without inward

* Hall (American Association Address, 1857, subsequently republished, with additions, as "Contributions to the Geological History of the American Continent," Mallet), Rogers, Dana, Le Conte, &c.

† See recent papers of Oldham and Fisher in *Geological Magazine* and *Philosophical Magazine*, July, 1886. Also Péroche, "Revol. Polaires," Paris, 1886.

* Address to the Geological Section, by Prof. Judd, Aberdeen Meeting, 1885. According to Rogers, the Crumpling of the Appalachians has reduced a breadth of 158 miles to about 60.

in successive layers.* (2) *Exoplutonic*, or that which considers them as made up of matter ejected from below the upper crust in the manner of volcanic action.† (3) *Metamorphic*, which supposes the old gneisses to arise from the crystallisation of detrital matter spread over the seabottom, and either igneous or derived from the decay of igneous rocks.‡ (4) *Chaotic* or *Thermo-chaotic*, or the theory of deposit from the turbid waters of a primeval ocean either with or without the aid of heat. In one form this was the old theory of Werner.§ (5) *Crenitic* or *Hydro-thermic*, which supposes the action of heated waters penetrating below the crust to be constantly bringing up to the surface mineral matters in solution and depositing these so as to form felspathic and other rocks.¶

It will be observed, in regard to these theories, that none of them supposes that the old gneiss is an ordinary sediment, but that all regard it as formed in exceptional circumstances, these circumstances being the absence of land and of sub-aërial decay of rock, and the presence wholly or principally of the material of the upper surface of the recently hardened crust. This being granted, the question arises, Ought we not to combine these several theories and to believe that the cooling crust has hardened in successive layers from without inward; that at the same time fissures were locally discharging igneous matter to the surface: that matter held in suspension in the ocean and matter held in solution by heated waters rising from beneath the outer crust were mingling their materials in the deposits of the primitive ocean? It would seem that the combination of all these agencies may safely be invoked as causes of the pre-Atlantic deposits. This is the eclectic position which I endeavoured to maintain in my address before the Minneapolis Meeting of the American Association in 1883, and which I still hold to be in every way probable.

A word here as to metamorphism, a theory which, like many others, has been first run to death and then discredited, but which to the moderate degree in which it was originally held by Lyell is still valid. Nothing can be more certain than that the composition of the Laurentian gneisses forbids us to suppose that they can be ordinary sediments metamorphosed. They are rocks peculiar in their origin, and not paralleled unless exceptionally in later times. On the other hand, they have undoubtedly experienced very important changes, more especially as to crystallisation, the state of combination of their ingredients, and the development of disseminated minerals;¶ and while this may in part be attributed to

the mechanical pressure to which they have been subjected, it requires also the action of hydrothermic agencies. Any theory which fails to invoke both of these kinds of force must necessarily be partial and imperfect.

But all metamorphic rocks are not of the same character with the gneisses of the Lower Laurentian. Even in the Middle and Upper Laurentian we have metamorphic rocks, e.g. quartzite and limestone, which must originally have been ordinary aqueous deposits. Still more in the succeeding Huronian and its associated series of beds, and in the Lower Palæozoic, local metamorphic change has been undergone by rocks quite similar to those which in their unaltered state constitute regular sedimentary deposits. In the case of these later rocks it is to be borne in mind that, while some may have been of volcanic origin, others may have been sediments rich in undecomposed fragments of silicates. It is a mistake to suppose that the ordinary decay of stratified siliceous rocks is a process of kaolinisation so perfect as to eliminate all alkaline matters. On the contrary, the fact, which Judd has recently well illustrated in the case of the mud of the Nile, applies to a great number of similar deposits in all parts of the world, and shows that the finest sediments have not always been so completely lixiviated as to be destitute of the basic matters necessary for their conversion into gneiss, mica-schist, and similar rocks when the necessary agencies of metamorphism are applied to them, and this quite independently of any extraneous matters introduced into them by water or otherwise. Still it must be steadily kept in view that many of the old pre-Cambrian crystalline rocks must have been different originally from those succeeding them, and that consequently these last even when metamorphosed present different characters.

(To be continued.)

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.,
President of the Section.

A GLANCE over the Presidential Addresses delivered before this Section on former occasions will show that the occupiers of this chair have ranged over a fairly wide field. Some of my predecessors have given a general survey of the progress of chemical science during the past year; some, taking up a technological aspect of the subject, have discussed the bearings of chemistry upon our national industries; others, again, have passed in review the various institutions in this country for teaching chemistry; and in yet other cases the speaker has had the opportunity of bringing before the scientific world, for the first time, an account of some important original researches.

On this occasion I venture to ask your attention to a few thoughts on the very foundations of chemistry as a science,—on the nature and the probable, or at least possible, origin of the so called elements. If the views to which I have been led may at first glance appear heretical, I must remind you that in some respects they are shared more or less, as I shall subsequently show, by not a few of the most eminent authorities, and notably by one of my predecessors in this chair, Dr. J. H. Gladstone, F.R.S., to whose brilliant address, delivered in 1883, I must beg to refer you.

Should it not sometimes strike us, chemists of the present day, that after all we are in a position unpleasantly akin to that of our forerunners, the alchemists of the Middle Ages? These necromancers of a time long past did not, indeed, draw so sharp a line as do we between bodies

* Naumann, Phillips, Durocher, McFarlane, &c.

† Clarence King, Tornebohm, Marr, &c.

‡ Lyell, Kopp, Reusch, Judd, &c.

§ Scrope, Delabèche, Daubrée.

¶ Hunt, *loc. cit.* The following is Dr. Hunt's summary statement of this theory:—"The globe consolidating at the centre left, it is conceived, a superficial layer of basic silicates, which has yielded all the fixed elements of the earth's crust. This layer formed the first land and the floor of the primeval sea, the acid waters of which, permeating and partially decomposing it, became thereby chemically neutralised. This last-cooled layer, mechanically disintegrated, saturated with water, and heated by the central mass, was the source of mineral springs, holding in solution the silicates which built up the ancient gneisses and similar rocks. Granitic veins and zeolites are due to survivals of the process which generated the gneissic rocks. The hypothesis of their formation from materials brought to the surface by mineral springs from the primitive basic layer affords, it is claimed, the elements of a complete and intelligible explanation of the origin of the Eozoic rocks. This upward lixiviation of the primitive mass, and the deposition over it of an acidic granite-like rock, would leave below a highly basic material, and the division of the mass thus established would correspond to that of the trachytic and doleritic magmas, which have been conjectured to be the sources of two great types of eruptive rocks. Inasmuch, however, as according to the present hypothesis these two layers of basic and acidic matters are the results of aqueous action, and not of an original separation in a plutonic mass, as imagined by Phillips and Durocher, their composition would be subject to many local variations."

¶ The first of these is what Bonney has called *Metastasis*. The second and third come under the name *Metacrisis*. *Methylosis*, or change of substance, is altogether exceptional, and not to be credited except on the best evidence, or in cases where volatile matters have been expelled, as in the change of hematite into magnetite, or of bituminous coal into anthracite.

simple and compound; yet their life-task was devoted to the formation of new combinations, and to the attempt to transmute bodies which we commonly consider as simple and ultimate,—that is, the metals. In the department of synthesis they achieved very considerable successes; in the transmutation of metals their failure is a matter of history.

But what are we of this so-called Nineteenth Century doing in our laboratories and our libraries? Too many of us are content to acquire simply what others have already observed and discovered, with an eye directed mainly to medals, certificates, diplomas, and other honours recognised as the fruits of "passing." Others are seeking to turn the determined facts of chemistry to useful purposes; whilst a third class, sometimes not easily distinguished from the second, are daily educating novel organic compounds, or are racking their ingenuity to prepare artificially some product which Nature has hitherto furnished us through the instrumentality of plants and animals. The practical importance of such investigations, and their bearing on the industrial arts and on the purposes and needs of daily life, have been signally manifested during the last half century.

Still a fourth class of inquirers working at the very confines of our knowledge, find themselves occasionally at least face to face with a barrier which has hitherto proved impassable, but which must be overthrown, surmounted, or turned if chemical science is ever to develop into a definite, an organised unity. This barrier is nothing less than the chemical elements commonly so called, the bodies as yet undecomposed into anything simpler than themselves. There they extend before us, as stretched the wide Atlantic before the gaze of Columbus, mocking, taunting, and murmuring strange riddles, which no man yet has been able to solve.

The first riddle, then, which we encounter in chemistry is "What are the elements?" Of the attempts hitherto made to define or explain an element none satisfy the demands of the human intellect. The text-books tell us that an element is "a body which has not been decomposed;" that it is "a something to which we can add, but from which we can take away nothing," or "a body which increases in weight with every chemical change." Such definitions are doubly unsatisfactory: they are provisional, and may cease to-morrow to be applicable in any given case. They take their stand, not on any attribute of the things to be defined, but on the limitations of human power; they are confessions of intellectual impotence.

Just as to Columbus long philosophic meditation led him to the fixed belief of the existence of a yet untrodden world beyond that waste of Atlantic waters, so to our most keen-eyed chemists, physicists, and philosophers a variety of phenomena suggest the conviction that the elements of ordinary assumption are not the ultimate boundary in this direction, of the knowledge which man may hope to attain. Well do I remember, soon after I had obtained evidence of the distinct nature of thallium, that Faraday said to me—"To discover a new element is a very fine thing, but if you could decompose an element and tell us what it is made of,—that would be a discovery indeed worth making." And this was no new speculation of Faraday's, for in one of his early lectures he remarked—"At present we begin to feel impatient, and to wish for a new state of chemical elements. For a time the desire was to add to the metals, now we wish to diminish their number. . . . To decompose the metals, then, to reform them, to change them from one to another, and to realise the once absurd notion of transmutation are the problems now given to the chemist for solution."

Mr. Herbert Spencer, in his hypothesis of the constitution of matter, says:—"All material substances are divisible into so-called elementary substances composed of molecular particles of the same nature as themselves; but

these molecular particles are complicated structures consisting of congregations of truly elementary atoms, identical in nature and differing only in position, arrangement, motion, &c., and the molecules or chemical atoms are produced from the true or physical atoms by processes of evolution under conditions which chemistry has not yet been able to reproduce."

Mr. Norman Lockyer has shown, I think on good evidence, that, in the heavenly bodies of the highest temperature, a large number of our reputed elements are dissociated, or, as it would perhaps be better to say, have never been formed. Mr. Lockyer holds that "The temperature of the sun and the electric arc is high enough to dissociate some of the so-called chemical elements, and give us a glimpse of the spectra of their bases"; and he likewise says that "A terrestrial element is an exceedingly complicated thing that is broken up into simpler things at the temperature of the Sun, and some of these things exist in some sun-spots, while other constituents exist in others."

The late Sir Benjamin Brodie, in a lecture on Ideal Chemistry delivered before the Chemical Society in 1867, goes even further than this. He says:—"We may conceive that, in remote time or in remote space, there did exist formerly, or possibly do exist now, certain simpler forms of matter than we find on the surface of our globe— α , χ , ξ , ν , and so on. . . . We may consider that in remote ages the temperature of matter was much higher than it is now, and that these other things existed then in the state of perfect gases—separate existences—uncombined. . . . We may then conceive that the temperature began to fall, and these things to combine with one another and to enter into new forms of existence, appropriate to the circumstances in which they were placed. . . . We may further consider that, as the temperature went on falling, certain forms of matter became more permanent and more stable, to the exclusion of other forms. . . . We may conceive of this process of the lowering of the temperature going on, so that these substances, when once formed, could never be decomposed—in fact, that the resolution of these bodies into their component elements could never occur again. You would then have something of our present system of things. . . ."

"Now this is not purely an imagination, for when we look upon the surface of our globe we have actual evidence of similar changes in Nature. . . . When we look at some of the facts which have been revealed to us by the extraordinary analyses which have been made of the matter of distant worlds and nebulae, by means of the spectroscopic, it does not seem incredible to me that there may even be evidence, some day, of the independent existence of such things as χ and ν ."

In his Burnett Lectures "On Light as a Means of Investigation," Professor Stokes, speaking of a line in the spectrum of the nebulae, says:—"It may possibly indicate some form of matter more elementary than any we know on earth. There seems no *a priori* improbability in such a supposition so great as to lead us at once to reject it. Chemists have long speculated on the so-called elements, or many of them, being merely very stable compounds of elements of a higher order, or even perhaps of a single kind of matter."

In 1868, Graham wrote of Sir W. Thomson's vortex-ring theory, as enlivening "matter into an individual existence and constituting it a distinct substance or element."

From these passages, which might easily be multiplied, it plainly appears that the notion—not necessarily of the decomposability, but at any rate of the complexity of our supposed elements—is, so to speak, in the air of science, waiting to take a further and more definite development. It is important to keep before men's minds the idea of the genesis of the elements; this gives some form to our conceptions, and accustoms the mind to look for some physical production of atoms. It is still more important, too, to keep in view the great probability that there exist

in Nature laboratories where atoms are formed and laboratories where atoms cease to be. We are on the track and are not daunted, and fain would we enter the mysterious region which ignorance tickets "Unknown." It is for us to strive to unravel the secret composition even of the so-called elements,—to undauntedly persevere,—and "still bear up right onward."

If we adopt the easy-going assumption that the elements, whether self-existent or created, are absolutely and primordially distinct; that they existed as we now find them prior to the origin of stars and their attendant planets, constituting, in fact, the primal "fire-mist," we are little, if any, the wiser. We look at their number and at their distinctive properties, and we ask, Are all these points accidental or determinate? In other words, might there as well have been only 7, or 700, or 7000 absolutely distinct elements as the 70 (in round numbers) which we now commonly recognise? The number of the elements does not, indeed, commend itself to our reason from any *à priori* or extraneous considerations. Might their properties have conceivably differed from those which we actually observe? Are they formed by a "fortuitous concatenation," or do they constitute together a definite whole, in which each has its proper part to play, and from which none could be extruded without leaving a recognizable deficiency?

If their peculiarities were accidental it would scarcely be possible for the elements to display those mutual relations which we find brought into such prominent light and order in the periodic classification of Newlands, Mendeleeff, and Meyer. Has not the relation between the atomic weights of the three halogens, chlorine, bromine, and iodine, and their serially varying properties, physical and chemical, been worn nearly threadbare? And the same with the calcium and the sulphur groups? Surely the probability of such relations existing among some 70 bodies which had come into fortuitous existence would prove to be vanishingly small!

We ask whether these elements may not have been evolved from some few antecedent forms of matter,—or possibly from only one such—just as it is now held that all the innumerable variations of plants and animals have been developed from fewer and earlier forms of organic life? As Dr. Gladstone well puts it, they "have been built up one from another, according to some general plan." This building up, or evolution, is above all things not fortuitous: the variation and development which we recognise in the universe run along certain fixed lines which have been preconceived and fore-ordained. To the careless and hasty eye design and evolution seem antagonistic; the more careful inquirer sees that evolution, steadily proceeding along an ascending scale of excellence, is the strongest argument in favour of a preconceived plan.

The array of the elements cannot fail to remind us of the general aspect of the organic world. In both cases we see certain groups well filled up, even crowded with forms having among themselves but little specific difference. On the other hand, in both, other forms stand widely isolated. Both display species that are common and species that are rare; both have groups widely distributed,—it might be said cosmopolitan, and other groups of very restricted occurrence. Among animals I may mention as instances the Monotremata of Australia and New Guinea, and among the elements the metals of the so-called rare earths.

Now as these facts in the distribution of organic forms are generally considered by biological experts to rank among the weightiest evidences in favour of the origin of species by a process of evolution, it seems natural, in this case as in the other, to view existing elements not as primordial but as the gradual outcome of a process of development, possibly even of a "struggle for existence." Bodies not in harmony with the present general conditions have disappeared or perhaps have never

existed. Others—the asteroids among the elements—have come into being and have survived, but only on a limited scale; whilst a third class are abundant because surrounding conditions have been favourable to their formation and preservation.

The analogy here suggested between elements and organisms is, indeed, not the closest, and must not be pushed too far. From the nature of the case there cannot occur in the elements a difference corresponding to the difference between living and fossil organic forms. The "great stone book" can tell us nothing of extinct elements. Nor would I for a moment suggest that any one of our present elements, however rare, is like a rare animal or plant in process of extinction; that any new element is in the course of formation, or that the properties of existing elements are gradually undergoing modification. All such changes must have been confined to that period so remote as not to be grasped by the imagination, when our Earth, or rather the matter of which it consists, was in a state very different from its present condition. The epoch of elemental development is decidedly over, and I may observe that in the opinion of not a few biologists the epoch of organic development is verging upon its close.

Making, however, every allowance for these distinctions, if evolution be a cosmic law, manifest in heavenly bodies, in organic individuals, and in organic species, we shall in all probability recognise it, though under especial aspects, in those elements of which stars and organisms are in the last resort composed.

Is there then, in the first place, any direct evidence of the transmutation of any supposed "element" of our existing list into another, or of its resolution into anything simpler?

To this question I am obliged to reply in the negative.

I doubt whether any chemist here present could suggest a process which would hold out a reasonable prospect of dissociating any of our accepted simple bodies. The highest temperatures and the most powerful electric currents at our disposal have been tried, and tried in vain. At one time there seemed a possibility at least that the interesting researches of Prof. Victor Meyer might show the two higher members of the halogen group, bromine and iodine, as entering upon the path of dissociation. These hopes have not been fulfilled. It may be said, in the general opinion of the most eminent and judicious chemists, that none of the phenomena thus elicited prove that even an approach has been made to the object in view.

Even if we leave our artificial laboratories and seek an escape from the difficulty by observing the processes of the great laboratories of nature, we feel no sufficiently firm ground.

We find ourselves thus driven to indirect evidence,—to that which we may glean from the mutual relations of the elementary bodies. Such evidence of great value is by no means lacking, and to this I now beg to direct attention. First, we may consider the conclusion arrived at by Herschel, and pursued by Clerk-Maxwell, that atoms bear the impress of manufactured articles. Let us look a little more closely at this view. A manufactured article may well be supposed to involve a manufacturer. But it does something more: it implies certainly a raw material, and probably, though not certainly, the existence of by-products, residues, *paraleipomena*. What or where is here the raw material? Can we detect any form of matter which bears to the chemical elements a relation like that of a raw material to the finished product, like that, say, of coal-tar to alizarin? Or can we recognise any elementary bodies which seem like waste or refuse? Or are all the elements, according to the common view, co-equals? To these questions no direct answer is as yet forthcoming.

And this leads us up to a hypothesis which, if capable of

full demonstration, would show us that the accepted elements are not co-equal, but have been formed by a process of expansion or evolution. I refer to the well-known hypothesis of Prout, which regards the atomic weights of the elements as multiples, by a series of whole numbers, of unity = the atomic weight of hydrogen. Every one is aware that the recent more accurate determinations of the atomic weights of different elements do not by any means bring them into close harmony with the values which Prout's law would require. Still, in no small number of cases the actual atomic weights approach so closely to those which the hypothesis demands, that we can scarcely regard the coincidence as accidental. Accordingly, not a few chemists of admitted eminence consider that we have here an expression of the truth, masked by some residual or collateral phenomena which we have not yet succeeded in eliminating.

The original calculations on which the most accurate numbers for the atomic weights are founded have recently been re-calculated by Mr. F. W. Clarke. In his concluding remarks, speaking of Prout's law, Mr. Clarke says that "none of the seeming exceptions are inexplicable. In short, admitting half multiples as legitimate, it is more probable that the few apparent exceptions are due to undetected constant errors than that the great number of close agreements should be merely accidental. I began this re-calculation of the atomic weights with a strong prejudice against Prout's hypothesis, but the facts as they came before me have forced me to give it a very respectful consideration."

But if the evidence in favour of Prout's hypothesis in its original guise is deemed insufficient, may not Mr. Clarke's suggestion of half multiples place it upon an entirely new basis? Suppose that the unit of the scale, the body whose atomic weight, if multiplied by a series of whole numbers, gives the atomic weights of the remaining elements, is not hydrogen, but some element of still lower atomic weight? We are here at once reminded of helium,—an element purely hypothetical as far as our earth is concerned, but supposed by many authorities, on the faith of spectroscopic observations, to exist in the sun and in other stellar bodies. Most solar eruptions present merely the characteristic lines of hydrogen C, F, and H, and along with them one particular line which at first was classed in the sodium group, but which is a little more refrangible and is designated by the symbol D_3 . According to Mr. Norman Lockyer and the late Father Secchi, this ray undergoes modifications not comparable to those affecting other rays of the chromosphere. In the corresponding region of the spectrum no dark ray has been observed. That the accompanying lines C, F, and H pertain to hydrogen is evident; and as D_3 has never been obtained in any other spectrum it is supposed to belong to a body foreign to our earth, though existing in abundance in the chromosphere of the sun. To this hypothetical body the name helium is assigned.

In an able memoir on this subject read before the Academy of Brussels, the Abbé E. Spée shows that, if helium exists, it enjoys two very remarkable properties. Its spectrum consists of a single ray, and its vapour possesses no absorbent power. The simple single ray, though I believe unexampled, is by no means an impossible phenomenon, and indicates a remarkable simplicity of molecular constitution. The non-absorbent property of its vapour seems to be a serious objection to a general physical law. Professor Tyndall has demonstrated that the absorptive power increases with the complexity of molecular structure, and hence he draws the conclusion that the simpler the molecule the feebler the absorption. This conclusion the Abbé Spée regards as perfectly legitimate; but it neither explains nor even necessitates the absence of all absorptive power.

Granting that helium exists, all analogy points to its atomic weight being below that of hydrogen. Here, then, we may have the very element with atomic weight

half that of hydrogen, required by Mr. Clarke as the basis of Prout's law.

But a more important piece of evidence for the compound nature of the chemical elements has yet to be considered. Many chemists must have been struck with certain peculiarities in the occurrence of the elements in the earth's crust; it is a stale remark that we do not find them evenly distributed throughout the globe. Nor are they associated in accordance with their specific gravities; the lighter elements placed on or near the surface, and the heavier ones following serially deeper and deeper. Neither can we trace any distinct relation between local climate and mineral distribution. And by no means can we say that elements are always or chiefly associated in Nature in the order of their so-called chemical affinities; those which have a strong tendency to form with each other definite chemical combinations being found together, whilst those which have little or no such tendency exist apart. We certainly find calcium as carbonate and sulphate, sodium as chloride, silver and lead as sulphides; but why do we find certain groups of elements with little affinity for each other yet existing in juxtaposition or commixture? The members of some of these groups are far from plentiful, not generally or widely diffused, and certainly they are not easy to separate.

As instances of such grouping we may mention:—

1. Nickel and cobalt, of which it may be said that had their compounds been colourless they would have been long regarded as identical, and possibly even yet would not have been separated.

2. The two groups of platinum metals.

3. The so-called "rare earths," occurring in gadolinite, samarskite, &c., and evidently becoming more numerous the more closely they are examined.

Certain questions here suggest themselves:—Is the series of these elements like a staircase or like an inclined plane? Will they, the more closely they are scrutinised, be found to fade away the more gradually the one into the other? Further, will a mixture hitherto held to be simple, like (*e.g.*) didymium, be capable of being split up in one direction only, or in several? I have been led to ask this last question because I have separated from didymium bodies which seems to agree neither with the praseodymium and neodymium of Dr. Auer von Welsbach, nor with the components detected by M. de Boisbaudran and M. Demarçay.

Why, then, are these respective elements so closely associated? What agency has brought them together?

An eminent physicist evades the difficulty by suggesting that their joint occurrence is simply an instance of the working of the familiar principle "Birds of a feather flock together." In their chemical and physical attributes these rare earths are so closely similar, that they may be regarded as substantially identical in all the circumstances of solution and precipitation to which they may have been exposed during Geological ages.

But do we, in point of fact, recognise any such agency at work in Nature? Is there any power which regularly and systematically sorts out the different kinds of matter from promiscuous heaps, conveying like to like and separating unlike from unlike? I must confess that I fail to trace any such distributive agency, nor, indeed, do I feel able to form any distinct conception of its nature.

I must here remark that coral worms in some cases do effect a separation of certain kinds of matter. Thus a *Gorgonia* of the species *Melithæa*, and *Mussa sinuosa*, undoubtedly eliminate from sea-water not merely lime, but even yttria; and other recent corals, *Pocillopora damicornis*, and a *Symphyllia* close to the yttria-secreting *Mussa*, separate samaria from sea-water. Sea-weeds and aquatic mollusks contain a larger proportion of iodine and bromine than the waters which they inhabit, and may thus be said to separate out these elements from the chlorine with which they are mingled.

But if we examine these cases of elimination we see that they are limited in their scope. They extend only to substances existing in solution of which there is a fresh supply always at hand, and which are capable of entering into the animal or vegetable economy. Again, the elimination of iodine and bromine, effected as just described, is of a very imperfect character, and, when such water-plants and animals die and decay, their constituents will be again distributed in the water.

We cannot well consider that nickel and cobalt have been deposited in admixture by organic agency, nor yet the groups iridium, osmium, and platinum,—ruthenium, rhodium, and palladium.

Since the earthy metals to which I have referred—such as yttrium, samarium, holmium, erbium, thulium, ytterbium, &c.—are very rare, the probability of their ever having been brought together in some few uncommon minerals discovered only in a few localities must be regarded as trifling indeed, if we suppose that these metals had at any time been widely diffused in a state of great dilution with other matter. The features which we have just recognised in these earths seem to point to their formation severally from some common material placed in conditions in each case nearly identical. The case is strengthened by a consideration of the other groups of elements, also similar in properties, having little affinity for each other and occurring in admixture; either all or at least some of the elements concerned being moreover decidedly rare. Thus we have nickel and cobalt not plentiful or widely distributed; cobalt, perhaps, never found absolutely free from nickel, and *vice versa*. We have also the two platinum groups, where very similar features prevail.

A weighty argument in favour of the compound nature of the elements is that drawn from a consideration of the compound radicles, or, as they might be called, pseudo-elements. Their similarity with the accepted elements is perfectly familiar to all chemists. If, for example, we suppose, that in some age or in some country men of science were cognizant of the existence and of the behaviour of cyanogen, but had not succeeded in resolving it into its constituents, nothing, surely, would prevent their viewing it as an element, and assigning it a place with the halogens. It may fairly be held that if a body which we know to be compound can be found playing the part of an element, this fact lends a certain plausibility to the supposition that the elements also are not absolutely simple. This line of thought, or at least one closely approximating to it, was worked out by Dr. Carnelley in a paper read before this Association at its last meeting. From a comparison of the physical properties of inorganic with those of organic compounds, Dr. Carnelley concludes that "*the elements, as a whole, are analogous to the hydrocarbon radicals.*" This conclusion, if true, he adds, should lead to the further inference that the so-called elements are not truly elementary, being made up of at least two absolute elements, named provisionally A and B. Hence, he argues, it should be possible to build up a series of compounds of these two primary elements which would correspond to what we now call elements. Such an arrangement, to be admissible, would have to fulfil certain conditions:—The secondary elements thus generated from A and B must exhibit the phenomena of periodicity, and the series would have to form octaves; the entire system is bound to display some feature corresponding to the "odd and even series" of Mendeleeff's classification; the atomic weights must increase across the system from the first to the seventh group,—that is, from the positive to the negative end of each series; the atomicity would have to increase from the first to the middle group, and then either increase or decrease to the seventh group; some feature should appear corresponding to the eighth group; and, lastly, the atomic weights in such a system ought to agree with the atomic weights as experimentally determined.

This last condition Dr. Carnelley rightly regards as the

most crucial, and he finds his arrangement gives atomic weights which in a majority of instances coincide approximately with the actual atomic weights. Thus out of a total of sixty-one elements whose atomic weights have been determined with at least approximate accuracy, and whose places in the periodic system is not disputed, twenty-seven agree almost exactly with the actual numbers, whilst nineteen others are not more than one unit astray.

For a detailed consideration of the conclusions which follow from Dr. Carnelley's views I must refer to his paper as read at our last meeting. Two points bear more especially upon the subject now under consideration,—that is, if this speculation on the genesis of the elements is well-founded. First, the existence of elements of identical atomic weights, isomeric with each other, would be possible; as such Dr. Carnelley mentions respectively nickel and cobalt (now found to have slightly different atomic weights) rhodium and ruthenium, osmium and iridium, and the metals of some of the rare earths. Secondly, in Dr. Carnelley's scheme all the chemical elements save hydrogen are supposed to be composed of two simpler elements, $A=12$ and $B=-2$. Of these he regards A as a tetrad identical with carbon, and B as a monad of negative weight—perhaps the ethereal fluid of space.

Dr. Carnelley's three primary elements therefore are carbon, hydrogen, and the ether.

Starting from the supposition that pristine matter was once in an intensely heated condition, and that it has reached its present state by a process of free cooling, Dr. E. J. Mills suggests that the elements, as we now have them, are the result of successive polymerisations. Dr. Mills reminds us that chemical substances in the process of cooling naturally increase in density, and, if such increase be measured as a function of time or of temperature, we sometimes observe that there are critical points corresponding to the formation of new and well-defined substances. In this manner, ordinary phosphorus is converted into the red variety, I is transformed into I_2 , S_2 becomes S_6 , and NO_2 N_2O_4 . Among organic bodies styrol, in like manner, according to Dr. Mills, is converted into metastyrol, aldehyd into paraldehyd, the cyanates into cyanurates, and turpentine into metaterebenthene. At the critical points above referred to heat is liberated in especial abundance, and the bodies thus formed are known as polymers. If we could gradually cool down substances through a vast range of temperature, we should then probably discover a much greater number of such critical points, or points of multiple proportion, than we have been able to discover experimentally.

The heat given out in the act of polymerisation naturally reverses to some extent the polymerisation itself, and so causes a partial return to the previous condition of things. This forward and backward movement, several times repeated, constitutes "periodicity." Dr. Mills regards variable stars as instances, now in evidence, of the genesis of elementary bodies.

From a study of the classification of the elements, Dr. Mills is of opinion that the only known polymers of the primitive matter are arsenic, antimony, and perhaps erbium and osmium; whilst zirconium, ruthenium, samarium, and platinum approximate to the positions of other polymers. Hence, from this genetic view, these elements may be described as products of successive polymerisations.

I must now call attention to a method of illustrating the periodic law, proposed by my friend Prof. Emerson Reynolds, of the University of Dublin, which will here assist us. Prof. Reynolds points out that in each period the general properties of the elements vary from one to another with approximate regularity until we reach the seventh member, which is in more or less striking contrast with the first element of the same period, as well as with the first of the next. Thus chlorine, the seventh member

of Mendeleeff's third period, contrasts sharply both with sodium, the first member of the same series, and with potassium, the first member of the next series, whilst, on the other hand, sodium and potassium are closely analogous. The six elements whose atomic weights intervene between sodium and potassium vary in properties, step by step, until chlorine, the contrast to sodium, is reached. But from chlorine to potassium, the analogue of sodium,

transition-element to exhibit. If we examine a particular period—for instance, that one whose meso-element is silicon, we note :—*First*, that the three elements of lower atomic weight than silicon, viz., sodium, magnesium, and aluminium, are distinctly *electro-positive* in character, while those of higher atomic weight, viz., phosphorus, sulphur, and chlorine, are as distinctly *electro-negative*. Throughout the best-known periods this remarkable sub-

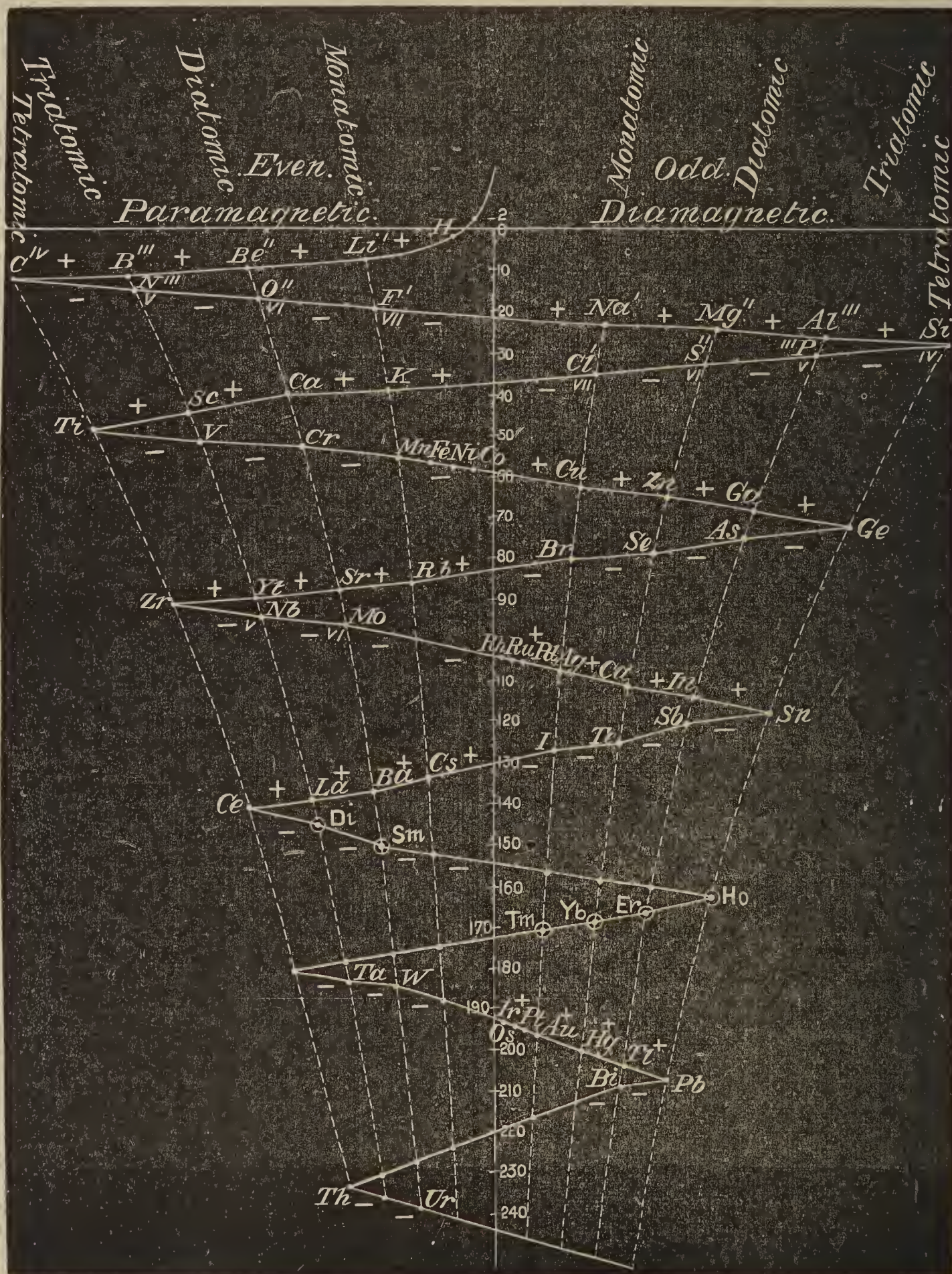


FIG. 1.

there is a change in properties *per saltum*. Further, such alternations of gradual and abrupt transitions are observed as the atomic weights increase. If we thus recognise a contrast in properties—more or less decided—between the first and the last members of each series, we can scarcely help admitting the existence of a point of mean variation within each system. In general, the *fourth* element of each series possesses the properties we might expect a

division is observable, although, as might be anticipated, the differences become less strongly marked as the atomic weights increase. *Secondly*, that the members above and below the meso-element fall into pairs of elements, which, while exhibiting certain analogies, are generally in more or less direct chemical contrast. Thus, in the silicon period we have—

	Si iv	
+Al'''		P''' —
+Mg''		S'' —
+Na'		Cl' —

This division also happens, in many cases, to coincide with some characteristic valence of the contrasted elements. It is noteworthy, however, that the members on the electro-negative side exhibit the most marked tendency to variation in atom-fixing power, so that valence alone is an untrustworthy guide to the probable position of an element in a period.

Thus for the purpose of graphic translation Professor Reynolds considers that the fourth member of a period—silicon, for example—may be placed at the apex of a symmetrical curve, which shall represent, for that particular period, the direction in which the properties of the series of elements vary with rising atomic weights.

In the drawing before you (Fig. 1) I have modified Prof. Reynolds's diagram in one or two points. I have turned it the reverse way, as it is more convenient to start from the top and proceed downwards.

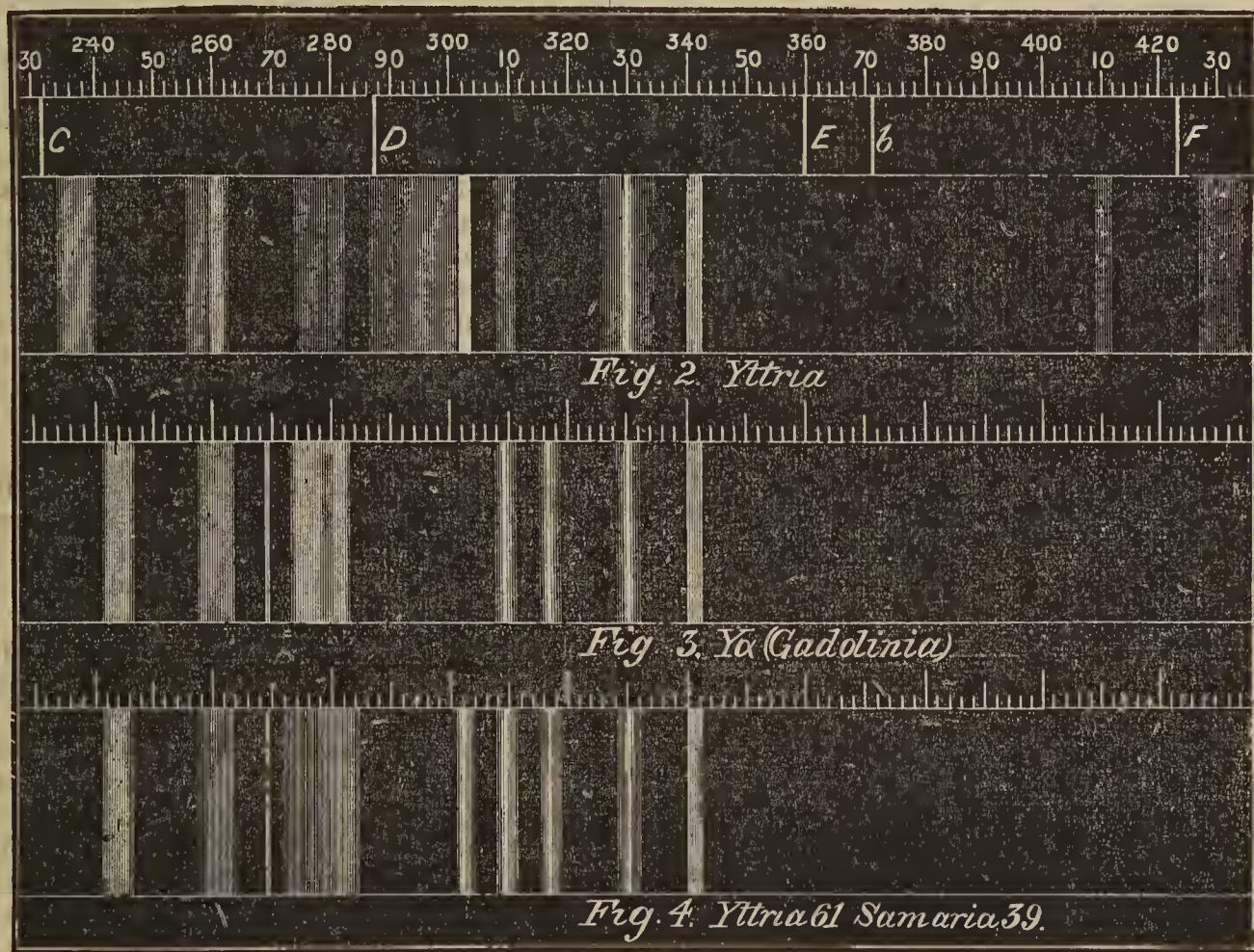
into which the other elements fall, and because their chemical relations with certain members of the adjacent periods show that they are probably interperiodic in the sense of being transitional.

This eighth group is divided into the three triplets—iron, nickel, and cobalt; rhodium, ruthenium, and palladium; iridium, osmium, and platinum. The members of each triplet have often been regarded as modifications of one single form of matter.

Notice how accurately the series of like bodies fits into this scheme. Beginning at the top, run the eye down analogous positions in each oscillation, taking either the electro-positive or electro-negative swings:—

N	Be	Li	Na	Mg	Al	Si	P	S	Cl	C
V	Ca	K	Cu	Zn	Ga	Ge	As	Se	Br	Ti
Nb	Sr	Rb	Ag	Cd	In	Sn	Sb	Te	I	Zr
—	Ba	Cs	—	—	—	—	—	—	—	—
Ta			Au	Hg	Tl	Pb	Bi			

Notice, also, how orderly the metals discovered by spectrum analysis fit in their places—gallium, indium, and thallium.



I have represented the pendulous swing as gradually declining in amplitude according to a mathematical law, and I have introduced another half-swing of the pendulum between cerium and lead, which not only renders the oscillations more symmetrical, but brings gold, mercury, thallium, lead, and bismuth on the side where they are in complete harmony with members of foregoing groups, instead of being out of harmony with them. This modification has another advantage, inasmuch as it leaves many gaps to be hereafter filled in with new elements just when the development of research is beginning to demand room for such expansion.

I do not, however, wish to infer that the gaps in Mendeleeff's table, and in this graphic representation of it, necessarily mean that there are elements actually existing to fill up the gaps; these gaps may only mean that at the birth of the elements there was an easy potentiality of the formation of an element which would fit into the place.

Following the curve from hydrogen downwards we find that the elements forming Mendeleeff's eighth group are to be found near three of the ten nodal points. These bodies are "interperiodic," both because their atomic weights exclude them from the small periods

The symmetry of nearly all this series proclaims at once that we are working in the right direction. We can also learn much from the anomalies here visible. Look at the places marked with a circle; didymium, samarium, holmium, erbium, ytterbium, and thulium. Didymium cannot follow in order after the triad nitrogen, vanadium, columbium; nor erbium follow phosphorus, arsenic, antimony; nor thulium follow chlorine, bromine, iodine; nor ytterbium follow potassium, rubidium, caesium. The inference to be drawn is that these bodies are out of place, owing to their atomic weights not having been correctly determined,—an inference which is strengthened by the knowledge that the elementary character of some of these bodies is more than doubtful, whilst the chemical attributes of most of them are unknown.

The more I study the arrangement of this zigzag curve the more I am convinced that he who grasps the key will be permitted to unlock some of the deepest mysteries of creation. Let us imagine if it is possible to get a glimpse of a few of the secrets here hidden. Let us picture the very beginnings of time, before geological ages, before the earth was thrown off from the central

nucleus of molten fluid, before even the sun himself had consolidated from the original *protyle*.* Let us still imagine that at this primal stage all was in an ultragaseous state, at a temperature inconceivably hotter† than anything now existing in the visible universe; so high, indeed, that the chemical atoms could not yet have been formed, being still far above their dissociation-point. In so far as *protyle* is capable of radiating or reflecting light, this vast sea of incandescent mist, to an astronomer in a distant star, might have appeared as a nebula, showing in the spectroscopic a few isolated lines, forecasts of hydrogen, carbon, and nitrogen spectra.

But in course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter as we know it comes into existence, and atoms are formed. As soon as an atom is formed out of *protyle* it is a store of energy, potential (from its tendency to coalesce with other atoms by gravitation or chemically) and kinetic (from its internal motions). To obtain this energy the neighbouring *protyle* must be refrigerated by it,‡ and thereby the subsequent formation of other atoms will be accelerated. But with atomic matter the various forms of energy which require matter to render them evident begin to act; and, amongst others, that form of energy which has for one of its factors what we now call *atomic weight*. Let us assume that the elementary *protyle* contains within itself the potentiality of every possible combining proportion or atomic weight. Let it be granted that the whole of our known elements were not at this epoch simultaneously created. The easiest formed element, the one most nearly allied to the *protyle* in simplicity is first born. Hydrogen,—or shall we say helium?—of all the known elements the one of simplest structure and lowest atomic weight, is the first to come into being. For some time hydrogen would be the only form of matter (as we now know it) in existence, and between hydrogen and the next formed element there would be a considerable gap in time, during the latter part of which the element next in order of simplicity would be slowly approaching its birth-point: pending this period we may suppose that the evolutionary process which soon was to determine the birth of a new element, would also determine its atomic weight, its affinities, and its chemical position.

In the original genesis, the longer the time occupied in that portion of the cooling down during which the hardening of the *protyle* into atoms took place, the more sharply defined would be the resulting elements; and, on the other hand, with more irregularity in the original cooling, we should have a nearer approach to the state of the elemental family such as we know it at present.

In this way it is conceivable that the succession of events which gave us such groups as platinum, osmium, and iridium,—palladium, ruthenium, and rhodium,—iron, nickel and cobalt, if the operation of genesis had been greatly more prolonged, would have resulted in the birth of only one element of these groups. It is also probable that by a much more rapid rate of cooling, elements would originate even more closely related than are nickel and cobalt, and thus we should have formed the nearly

allied elements of the cerium, yttrium, and similar groups; in fact the minerals of the class of samarskite and gadolinite may be regarded as the cosmical lumber-room where the elements in a state of arrested development—the unconnected missing links of inorganic Darwinism—are finally aggregated.

I have said that the original *protyle* contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits.

Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would be gradually bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which led up to it. I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's "old worn particles."

Is it not possible, or even feasible, that these heavier and lighter atoms may have been in some cases subsequently sorted out by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths.

This may seem an audacious speculation, but I do not think it is beyond the power of chemistry to test its feasibility. An investigation on which I have been occupied for several years has yielded results which to me appear apposite to the question, and I therefore beg permission here to allude briefly to some of the results, reserving details to a subsequent communication to the Section.

My work has been with the earths present in samarskite and gadolinite, separating them by systematic fractionation. Chemical fractionation, on which I hope to say more on another occasion, is very similar to the formation of a spectrum with a wide slit and a succession of shallow prisms. The centre portion remains unchanged for a long time, and the only approach to purity at first is at the two ends, while a considerable series of operations is needed to produce an appreciable change in the centre. The groups of didymium and yttrium earths are those which have chiefly occupied my attention. On comparing these rare earths we are at once struck with the close mutual similarity, verging almost into identity, of the members of the same group.

The phosphorescent spectra of these earths when their anhydrous sulphates are submitted to the induction discharge *in vacuo* are extremely complicated, and change in their details in a puzzling manner. For many years I have been persistently groping on in almost hopeless endeavour to get a clue to the meaning I felt convinced was locked up in these systems of bands and lines. It was impossible to divest myself of the conviction that I was looking at a series of autograph inscriptions from the molecular world, evidently of intense interest, but written in a strange and baffling tongue. All attempts to decipher the mysterious signs were, however, for a long time, fruitless. I required a Rosetta stone.

Down to a date comparatively recent nothing was more firmly fixed in my mind than the notion that yttria was the oxide of a simple body, and that its phosphorescent spectrum gave a definite system of coloured bands,

* We require a word, analogous to protoplasm, to express the idea of the original primal matter existing before the evolution of the chemical elements. The word I have ventured to use for this purpose is compounded of *πρῶ* (earlier than) and *ὕλη* (the stuff of which things are made). The word is scarcely a new coinage, for 600 years ago Roger Bacon wrote in his *De Arte Chymia*—"The elements are made out of *ὕλη*, and every element is converted into the nature of another element."

† I am constrained to use words expressive of high temperature; but I confess I am unable clearly to associate with *protyle* the idea of hot or cold. *Temperature*, *radiation*, and *free cooling* seem to require the periodic motions that take place in the chemical atoms; and the introduction of centres of periodic motion into *protyle* would constitute its being so far changed into chemical atoms.

‡ I am indebted to my friend G. Johnstone Stoney, F.R.S., for the idea here put forward, as well as for other valuable suggestions and criticisms on some of the theoretical questions here treated of.

such as you see in the drawing before you (Fig. 2). Broadly speaking, there is a deep red band, a red band, a very luminous citron-coloured band, a pair of greenish blue bands, and a blue band. It is true these bands varied slightly in relative intensities and in sharpness with almost every sample of yttria I examined; but the general character of the spectrum remained unchanged, and I had got into the way of looking upon this spectrum as characteristic of yttria: all the bands being visible when the earth was present in quantity, whilst only the strongest band of all—the citron band—was visible when traces, such as millionths, were present. But that the whole system of bands spelled yttria and nothing but yttria I was firmly convinced.

During the later fractionations of the yttria earths, and the continued observations of their spectra, certain suspicions which had troubled me for some time assumed consistent form. The bands which hitherto I had thought belonged to yttria began to vary in intensity among themselves, and continued fractionation increased the differences first observed. Whilst I was in this state of doubt and uncertainty, and only beginning to see my way towards arranging into a consistent whole the facts daily coming to light, help came from an unexpected quarter. M. de Marignac, with whom I had been for some time in correspondence, kindly sent me a small specimen of the earth which he had discovered and provisionally named *Y_a* (now gadolinia). In the radiant-matter tube this earth gave a bright spectrum like the one in the diagram before you (Fig. 3). The spectrum above it (Fig. 2) is that ascribed to yttria. Look at the two. Omitting minor details, *Y_a* is yttria with the chief characteristic band—the citron band—left out, and with the double green band of samaria added to it. Now look at Fig. 4, which represents the spectrum of a mixture of 61 parts of yttria and 39 parts of samaria. It is identical almost to its minutest detail with the spectrum of *Y_a*, with this not unimportant difference—the citron band is as prominent as any other line. *Y_a* consists, therefore, of samaria with the greenish blue of yttria and some of the other yttria bands added to it.

I may aptly call the *Y_a* spectrum my Rosetta stone. It threw a flood of light on all the obscurities and contradictions I had found so plentiful, and showed me that a much wider law than the one I had been working upon was the true law governing the occurrence of these obscure phenomena. For what does the spectrum of *Y_a* show? It proves that what I had hitherto thought was one of the chief bands in the yttria spectrum—the citron band—could be entirely removed, whilst another characteristic group—the double green of yttria—could also be separated from the citron.

It would exceed legitimate limits were I to enter into details respecting the chemical and physical reasons which led me to these definite conclusions. To settle one single point more than 2000 fractionations have been performed.

The meaning of the strongly marked symbolic lines had first to be ascertained. For a long time I had to be content with roughly translating one group of coloured symbols as "yttrium" and another group as "samarium," disregarding the fainter lines, shadows, and wings frequently common to both. Constant practice in the decipherment has now given me fuller insight into what I may call the grammar of these hieroglyphic inscriptions. Every line and shadow of a line, each faint wing attached to a strong band, and every variation in intensity of the shadows and wings among themselves, now has a definite meaning which can be translated into the common symbolism of chemistry.

In a mineral containing the rarer earths, those most widely separated in chemical properties are most easily obtained in a state of comparative purity by simple chemical means. For instance, in separating didymium from lanthanum, or samarium from yttrium, a few simple chemical reactions and a little waste will give these bodies in a

state of purity; but when it comes to splitting up yttrium into its components ordinary chemical separation is useless, and fractionation must be pushed to the utmost limit, many thousand operations and enormous waste of material being necessary to effect even a partial separation.

Returning therefore, after this explanatory digression, to the idea of heavy and light atoms, we see how well this hypothesis accords with the new facts here brought to light. From every chemical point of view the stable molecular group, yttrium, behaves as an element. Excessive and systematic fractionation has acted the part of a chemical "sorting Demon," distributing the atoms of yttrium into several groups, with certainly different phosphorescent spectra, and presumably different atomic weights, though all these groups behave alike from the usual chemical point of view. Here, then, is one of the elements the spectrum of which does not emanate equally from all its atoms, but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. And as this is the case with one element, it is probably so in a greater or less degree with all. Hence the atoms of this element differ probably in weight, certainly in the internal motions they undergo.

Another important inference which may be drawn from the facts is, that the atoms of which yttrium consists, though differing, do not differ continuously, but *per saltum*. We have evidence of this in the fact that the spectroscopic bands characteristic of each group are distinct from those of the other groups, and do not pass gradually into them. We must accordingly expect, in the present state of science, that this is probably the case with the other elements. And the atoms of a chemical element being known to differ in one respect may differ in other respects, and presumably do somewhat differ in mass.

Restricted by limited time and means, even a partial separation of these atomic groupings is possible to me only with enormous difficulty. Have we any evidence that Nature has effected such a separation? The following facts I think supply this evidence.

The earth yttria occurs in several minerals, all extremely rare. These minerals are of very diverse chemical composition, and occur in localities widely separated geographically. Does the pure yttria (*pure* in respect to every other known element) from these different sources behave differently to the radiant-matter test? To the chemist hitherto the earth yttria has been the same thing and has possessed the same properties whatever its source; but armed with this new power of seeing into the atomic groupings which go to make up yttrium, we find evidence of differentiation between one yttrium and another.

Thus when the samarskite yttrium was formed all the constituent atoms—deep red, red, orange, citron, greenish blue, and blue*—condensed together in fair proportion, the deep red being faintest. In gadolinite yttrium the citron and greenish blue constituents are plentiful, the red is very deficient, the orange is absent, and the others occur in moderate quantities. In the yttrium from xenotime the citron is most plentiful, the greenish blue occurs in smaller proportion, the red is all but absent, and the orange is quite absent. Yttrium from monazite contains the greenish blue and citron, with a fair proportion of the other constituents; the greenish blue is plentiful, and the red is good. Yttrium from fluocerite is very similar to that from monazite, but the blue is weaker. Yttrium from hielmite is very rich in citron, has a fair quantity of blue and greenish blue, less of red, no orange, and only a very faint trace of deep red. Yttria from euxenite is almost identical with that from hielmite. Yttria from cerite contains most red and citron, a fair amount of orange, less greenish blue and blue, and only a trace of deep red.

This is unlikely to be an isolated case. The principle

* For brevity I call them by their dominant spectrum band.

is very probably of general application to all the elements. In some, possibly in all elements, the whole spectrum does not emanate from all its atoms, but different spectral rays may come from different atoms, and in the spectrum as we see it all these partial spectra are present together. This being interpreted means that there are definite differences in the internal motions which go on in the several groups of which the atoms of a chemical element consist. For example, we must now be prepared for some such events as that the seven series of bands in the absorption-spectrum of iodine may prove not all to emanate from every molecule, but that some of these molecules emit some of these series, others others, and in the jumble of all these kinds of molecules, to which is given the name "iodine vapour," the whole seven series are contributors.

To me it appears the theory I have here ventured to formulate, taken in conjunction with the diagram in Fig. 1, may aid the scientific imagination to proceed a step or two further in the order of elemental evolution. In the undulating curve may be seen the action of two forces, one acting in the direction of the vertical line, and the other pulsating backwards and forwards like a pendulum. Assume the vertical line to represent temperature slowly sinking through an unknown number of degrees, from the dissociation point of the first-formed element down to the dissociation point of those last shown on the scale. But what form of energy is represented by the oscillating line? Swinging to and fro like a mighty pendulum to points equidistant from a neutral centre; the divergence from neutrality conferring atomicity of one, two, three, and four degrees as the distance from the centre is one, two, three, or four divisions; and the approach to, or retreat from, the neutral line deciding the electro-negative or electro-positive character of the element,—all on the retreating half of the swing being positive and all on the approaching half negative—this oscillating force must be intimately connected with the imponderable matter, essence, or source of energy we call electricity.

Let us examine this a little more closely. Let us start at the moment when the first element came into existence. Before this time matter, as we know it, was not. It is equally impossible to conceive of matter without energy, as of energy without matter; from one point of view the two are convertible terms. Before the birth of atoms all those forms of energy which become evident when matter acts upon matter, could not have existed,—they were locked up in the *protyle* as latent potentialities only. Coincident with the creation of atoms all those attributes and properties which form the means of discriminating one chemical element from another start into existence fully endowed with energy.

The pendulum begins its swing from the electro-positive side; lithium, next to hydrogen in simplicity of atomic weight, is now formed; then glucinum, boron, and carbon. Definite quantities of electricity are bestowed on each element at the moment of birth, on these quantities its atomicity depends,* and the types of monatomic, diatomic, triatomic, and tetratomic elements are fixed. The electro-negative part of the swing now commences; nitrogen appears, and notice how curiously position governs the mean dominant atomicity. Nitrogen occupies the position below boron, a triatomic element, therefore nitrogen is triatomic. But nitrogen also follows carbon, a tetratomic body, and

occupies the fifth position counting from the place of origin; how beautifully these opposing tendencies are harmonised by the endowment of nitrogen with at least a double atomicity, and making its atom capable of acting as tri- and pentatomic. With oxygen (di- and hexatomic) and fluorine (mon- and heptatomic) the same law holds, and one-half oscillation of the pendulum is completed. Again passing the neutral line the electro-positive elements sodium (monatomic), magnesium (diatomic), aluminium (triatomic), and silicon (tetratomic) are successively formed, and the first complete oscillation of the pendulum is finished by the birth of the electro-negative elements phosphorus, sulphur, and chlorine; these three—like the corresponding elements formed on the opposite homeward swing—having each at least a double atomicity depending on position.

Let us pause at the end of the first complete vibration and examine the result. We have already formed the elements of water, ammonia, carbonic acid, the atmosphere, plant and animal life, phosphorus for the brain, salt for the sea, clay for the solid earth, two alkalies, an alkaline earth, an earth, together with their carbonates, borates, nitrates, fluorides, chlorides, sulphates, phosphates, and silicates, sufficient for a world and inhabitants not so very different from what we enjoy at the present day. True the human inhabitants would have to live in a state of more than Arcadian simplicity, and the absence of calcic phosphate would be awkward as far as bone is concerned. But what a happy world it would be! No silver or gold coinage, no iron for machinery, no platinum for chemists, no copper wire for telegraphy, no zinc for batteries, no mercury for pumps, and, alas! no rare earths to be separated.

The pendulum does not, however, stop at the end of the first complete vibration; it crosses the neutral point, and now the forces at work are in the same position as they were at the beginning. Had everything been as it was at first the next element again would have been lithium, and the original cycle would have recurred, repeating for ever the same elements. But the conditions are not quite the same; the form of energy represented by the vertical line has declined a little,—the temperature has sunk,—and not lithium, but the one next allied to it in the series comes into existence,—potassium, which may be regarded as the lineal descendant of lithium, with the same hereditary tendencies, but with less molecular mobility and higher atomic weight.

Pass we rapidly along the to and fro curve, and in nearly every case the same law is seen to hold good. The last element of the first complete vibration is chlorine. In the corresponding place in the second vibration we do not have an exact repetition of chlorine, but the very similar body bromine; and when for a third time the position recurs we see iodine. I need not multiply examples.

In this far reaching evolutionary scheme it could not come to pass that the potential elements would all be equal to one another. Some would be unable to resist the slightest disturbance of the unstable equilibrium in which they took their rise; others would endure longer, but would ultimately break down as temperature and pressure varied. Many degrees of stability would be here represented; not all the chemical elements are equally stable, and if we look with scrutinising eyes we shall still see our old friend the missing link, coarse enough to be detected by ordinary chemical processes, associated in the groups containing such elements as iron, nickel, and cobalt; palladium, ruthenium, and rhodium; iridium, osmium, and platinum. Whilst in their more subtle form these missing links present themselves as representatives of the differences which I have detected and described between the atoms of the same chemical element.

Dr. Carnelley has pointed out that "those elements belonging to the even series of Mendeleeff's classification are always paramagnetic, whereas the elements belonging

* "Nature presents us with a single definite quantity of electricity . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases."—G. JOHNSTONE STONEY, "On the Physical Units of Nature." British Association Meeting, 1874, Section A. *Phil. Mag.*, May, 1881.

"The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion."—HELMHOLTZ, Faraday Lecture, 1881.

"Every monad atom has associated with it a certain definite quantity of electricity; every dyad has twice this quantity associated with it; every triad three times as much, and so on."—O. LODGE. —"On Electrolysis," "British Association Report," 1885.

to the odd series are always diamagnetic." On this curve the even series to the left, as far as can be ascertained, are paramagnetic, and, with a few exceptions, all to the right are diamagnetic. The very powerful magnetic metals, iron, nickel, cobalt, and manganese, occur close together on the proper side. The interperiodic groups of which palladium and platinum are examples, are said to be feebly magnetic, and if so they form the exceptions. Oxygen, which weight for weight is more magnetic than iron, comes near the beginning of the curve, while the powerfully diamagnetic metals, bismuth and thallium, are at the opposite end of the curve.

On the odd, or diamagnetic half, of the swing, the energy appears to have considerable regularity, whilst it is very irregular on the opposite side of the curve. Thus, between the extreme odd elements, silicon (28), germanium (73), tin (118), the missing element (163), and lead (208), there is a difference of exactly 45 units, conferring remarkable symmetry on one half of the curve. The differences on the even side are 36, 42, 51, 39, and 53 (giving the missing element between cerium and thorium an atomic weight of 180); these at first sight appear conformable to no law, but they become of great interest when it is seen that the mean difference of these figures is almost exactly the same as that on the other side of the curve,—viz., 44·2.

This uniformity of difference,—actual on the one side and average on the other,—brings out the important inference that, whilst on the odd side there has been little or no variation in the vertical force, minor irregularities have been the rule on the even side. That is to say, the fall of temperature has been very uniform on the odd side—where every element formed during this half of the vibration is the representative of a strongly marked group,—sodium, magnesium, aluminium, silicium, phosphorus, sulphur, and chlorine; whilst on the even side of the swing the temperature has sunk with considerable fluctuations, which have prevented the formation here of any well-marked groups of elements, with the exception of those of which lithium and glucinum are the types.

If we can thus trace irregularities in the fall of temperature can we also detect any variation in the force represented by the pendulous movement? I have assumed that this represents chemical energy. In the early formed elements we have those in which chemical energy is at its maximum intensity, while, as we descend, affinities for oxygen are getting less and the chemism is becoming more and more sluggish. Part may be due to the lower temperature of generation not permitting such molecular mobility in the elements, but there can be little doubt that the chemism-forming energy, like the fires of the cosmical furnace, is itself dying out. I have endeavoured to represent this gradual fading out by a diminution of amplitude, the curve being traced from a photographic record of the diminution of the arc of vibration of a body swinging in a resisting medium.

When we look on a curve of this kind there is a tendency to ask, what is there above and below the portion which is seen? At the lower end of our curve what is there to be noted? We see a great hiatus between barium (137) and iridium (192·5), which it seems likely will be filled up by the so-called rare elements. Judging from my own researches, it is probable that many of these earthy elements will be found included in one or more interperiodic groups, whilst the higher members of the calcium, the potassium, the chlorine, and the sulphur groups, together with the elements between silver and gold, cadmium and mercury, indium and thallium, and antimony and bismuth, are still waiting to be discovered. We now come to an oasis in the desert of blanks. Platinum, gold, mercury, thallium, lead, and bismuth, all familiar friends, form a close little group by themselves, and then after another desert space the list is closed with thorium (233) and uranium (240).

This oasis, and the blanks which precede and follow it, may be referred with much probability to the particular way in which our earth developed into a member of our

solar system. If this be so it may be that on our earth only these blanks occur, and not generally throughout the universe.

What comes after uranium? I should consider that there is little prospect of the existence of an element much lower than this. Look at the vertical line of temperature slowly sinking from the upper to the lower part of the curve; the figures representing the scale of atomic weights may be also supposed to represent, inversely, the scale of a gigantic pyrometer dipping into the cauldron where suns and worlds are in process of formation. Our thermometer shows us that the heat has been sinking gradually, and, *pari passu*, the elements formed have increased in density and atomic weight. This cannot go on for an indefinite extent. Below the uranium point the temperature may be so reduced that some of the earlier formed elements which have the strongest affinities are able to enter into combination among themselves, and the result of the next fall in temperature will then be—instead of elements lower in the scale than uranium—the combination of oxygen with hydrogen, and the formation of those known compounds the dissociation of which is not beyond the powers of our terrestrial sources of heat.

Let us now turn to the upper portion of the scheme. With hydrogen of atomic weight = 1, there is little room for other elements, save perhaps for hypothetical helium. But what if we get "through the looking-glass," and cross the zero-line in search of new principles,—what shall we find the other side of zero? Dr. Carnelley asks for an element of negative atomic weight; here is ample room and verge enough for a shadow series of such unsubstantialities. Helmholtz says that electricity is probably as atomic as matter*: is electricity one of the negative elements? and the luminiferous ether another? Matter, as we now know it, does not here exist; the forms of energy which are apparent in the motions of matter are as yet only latent possibilities. A substance of negative weight is not inconceivable.† But can we form a clear conception of a body which combines with other bodies in proportions expressible by negative quantities?

A genesis of the elements such as is here sketched out would not be confined to our little solar system, but would probably follow the same general sequence of events in every centre of energy now visible as a star.

Before the birth of atoms to gravitate towards one another, no pressure could be exercised; but at the outskirts of the fire-mist sphere, within which all is protyle,—at the shell on which the tremendous forces involved in the birth of a chemical element exert full sway,—the fierce heat would be accompanied by gravitation sufficient to keep the newly born elements from flying off into space. As temperature increases expansion and molecular motion increase, molecules tend to fly asunder, and their chemical affinities become deadened; but the enormous pressure of the gravitation of the mass of atomic matter outside what I may for brevity call the birth-shell would counteract this action of heat.

Beyond this birth-shell would be a space in which no chemical action could take place, owing to the temperature there being above what is called the dissociation-point for compounds. In this space the lion and the lamb would lie down together; phosphorus and oxygen would mix without union; hydrogen and chlorine would show no tendency to closer bonds; and even fluorine, that energetic gas which chemists have only isolated within the last month or two, would float about free and uncombined.

Outside this space of free atomic matter would be

* "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity."—HELMHOLTZ, Faraday Lecture, 1881.

† "I can easily conceive that there are plenty of bodies about us not subject to this intermutual action, and therefore not subject to the law of gravitation."—SIR GEORGE AIRY. "Faraday's Life and Letters," vol. ii., p. 354.

another shell, in which the formed chemical elements would have cooled down to the combination-point, and the sequence of events so graphically described by Mr. Mattieu Williams in "The Fuel of the Sun" would now take place, culminating in the solid earth and the commencement of geological time.

And now I must draw to a close, having exhausted not indeed my subject, but the time I may reasonably occupy. We have glanced at the difficulty of defining an element; we have noticed too the revolt of many leading physicists and chemists against the ordinary acceptation of the term element. We have weighed the improbability of their eternal self-existence, or their origination by chance. As a remaining alternative we have suggested their origin by a process of evolution like that of the heavenly bodies according to Laplace, and the plants and animals of our globe according to Lamarck, Darwin, and Wallace. In the general array of the elements, as known to us, we have seen a striking approximation to that of the organic world. In lack of direct evidence of the decomposition of any element, we have sought and found indirect evidence. We have taken into consideration the light thrown on this subject by Prout's law, and by the researches of Mr. Lockyer in solar spectroscopy. We have reviewed the very important evidence drawn from the distribution and collocation of the elements in the crust of our earth. We have studied Dr. Carnelley's weighty argument in favour of the compound nature of the so-called elements from their analogy to the compound radicals. We have next glanced at the view of the genesis of the elements; and, lastly, we have reviewed a scheme of their origin suggested by Professor Reynolds's method of illustrating the periodic classification.

Summing up all the above considerations we cannot, indeed, venture to assert positively that our so-called elements have been evolved from one primordial matter; but we may contend that the balance of evidence, I think, fairly weighs in favour of this speculation.

This, then, is the intricate question which I have striven to unfold before you, a question that I especially commend to the young generation of chemists, not only as the most interesting but the most profoundly important in the entire compass of our science.

I say deliberately and advisedly the *most interesting*. The doctrine of Evolution, as you well know, has thrown a new light upon and given a new impetus to every department of biology, leading us, may we not hope, to anticipate a corresponding awakening light in the domain of chemistry?

I would ask investigators not necessarily either to accept or to reject the hypothesis of chemical evolution, but to treat it as a provisional hypothesis; to keep it in view in their researches, to inquire how far it lends itself to the interpretation of the phenomena observed, and to test experimentally every line of thought which points in this direction. Of the difficulties of this investigation none can be more fully aware than myself. I sincerely hope that this my imperfect attempt may lead some minds to enter upon the study of this fundamental chemical question, and to examine closely and in detail what I, as if amidst the clouds and mists of a far distance, have striven to point out.

CORRESPONDENCE.

FUCHSINE.

To the Editor of the Chemical News.

SIR,—From his silence on the point which prompted my first letter, namely, the statement that "fuchsine is a name unpronounceable by every Englishman who is not a German scholar," I gather that your Reviewer has retired from his original position as untenable.

He now raises, among other less questionable defences, the objection that fuchsine is an inappropriate name, because fuchsia flowers contain twenty tones of colour which could not be dyed with magenta at all. This argument reminds one of the old riddle about the "cherry-coloured dog." It is true that there are black and white cherries, as well as red cherries; but the terms "cherry-colour," "rose-colour," "violet," &c., are always understood as applying to certain well-known shades. So fuchsine was named from the resemblance of its tint to that of the typical fuchsia flower. I do not say that fuchsine is the best name which can be found for rosaniline salts, and fully share your Reviewer's objection to the coining of a quasi-scientific name for a substance which is not an active or characteristic principle of the plant from which the name originated; but I do contend that fuchsine is a preferable name to magenta, and that the objection raised to it by your Reviewer on the ground of unpronounceability is absolutely without foundation.—I am, &c.,

ALFRED H. ALLEN.

August 25, 1886.

MISCELLANEOUS.

Royal Academy of Arts, Burlington House.—Professor of Chemistry: A. H. Church, M.A.—A course of Lectures on the Chemistry of Paints, of Painting Methods, and of Pictures, will be delivered in November and December, 1886.

The Chemical Laboratory of Wiesbaden.—The Chemical Laboratory at this place still enjoys a very large attendance. Besides the Director, Gen. Hofrath Professor Dr. R. Fresenius, there are engaged as teachers in the establishment Professor Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. F. Hueppe, and Architect Brahm. The assistants in the Laboratory, in the summer term 1886, were fourteen in number, and in the Versuchsstation two. In the summer term 1886 there were eighty students on the books: of these fifty-five are from Germany, five from England, five from Russia, four from France, three from North America, two from Switzerland, two from Sweden, two from Italy, one from Austro-Hungary, and one from Luxemburg. During the last term, besides the scientific researches, a great number of analyses were undertaken in the Laboratory and the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

Analysis of Ceylon Soils.—We have received a table of the results of a number of analyses of Ceylon soils from Mr. John Hughes, F.C.S. The samples which were submitted to analysis were selected by the Planters' Association, and represent the soils of a number of the best estates, amongst which are the Ragalla, Dambattenne, Rookwood, Dryburgh, Liddesdale, Pallekelle, &c., on which coffee, tea, cinchona, and cacao have respectively been planted. The samples were all in the air-dried condition, and, on being heated to 212° F., lost water in quantities varying from 4.244 per cent at Dryburgh to 1.218 per cent at Pallekelle. The insoluble silicates and quartz in each case being respectively 55.9 per cent and 79.878 per cent. The highest percentage of organic matter and combined water was found on the Ragalla estate in the Uda Fussellawa district, and amounted to 24.337 per cent. The general results seem to show that cacao will flourish in the poorer soils, the Pallekelle estate, on which this is grown containing only 4.8 per cent of organic matter, 79.8 per cent of quartz and insoluble silicates, and 0.114 per cent of nitrogen, while coffee and cinchona require a higher percentage of organic matter and nitrogen, the highest percentage of the latter being 0.521 per cent.

THE CHEMICAL NEWS.

VOL. LIV. No. 1398.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BIRMINGHAM MEETING, SEPTEMBER 1, 1886.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR J. WILLIAM DAWSON, C.M.G., M.A., LL.D., F.R.S.,
F.G.S., Principal and Vice-Chancellor of McGill
University, Montreal, Canada.*

(Concluded from p. 115).

THE ocean is a great equaliser of extremes of temperature. It does this by its great capacity for heat and by its cooling and heating power when passing from the solid into the liquid and gaseous states, and the reverse. It also acts by its mobility, its currents serving to convey heat to great distances or to cool the air by the movement of cold icy waters. The land, on the other hand, cools or warms rapidly, and can transmit its influence to a distance only by the winds, and the influence so transmitted is rather in the nature of a disturbing than of an equalising cause. It follows that any change in the distribution of land and water must affect climate, more especially if it changes the character or course of the ocean currents.†

At the present time the North Atlantic presents some very peculiar and in some respects exceptional features, which are most instructive with reference to its past history. The great internal plateau of the American continent is now dry land; the passage across Central America between the Atlantic and Pacific is blocked; the Atlantic opens very widely to the north; the high mass of Greenland towers in its northern part. The effects are that the great equatorial current running across from Africa, and embayed in the Gulf of Mexico, is thrown northward and eastward in the Gulf Stream, acting as a hot-water apparatus to heat up to an exceptional degree the western coast of Europe. On the other hand, the cold Arctic current from the Polar Seas is thrown to the westward, and runs down from Greenland past the American shore.‡ The pilot chart for June of this year shows vast fields of drift ice on the western side of the Atlantic as far south as the latitude of 40°. So far, therefore, the Glacial age in that part of the Atlantic still extends; this at a time when, on the eastern side of the Ocean, the culture of cereals reaches in Norway beyond the Arctic Circle. Let us inquire into some of the details of these phenomena.

The warm water thrown into the North Atlantic not only increases the temperature of its whole waters, but gives an exceptionally mild climate to Western Europe. Still the countervailing influence of the Arctic currents and the Greenland ice is sufficient to permit icebergs which creep down to the mouth of the Strait of Belle Isle, in the latitude of the South of England, to remain unmelted till the snows of a succeeding winter fall upon them. Now let us suppose that a subsidence of land in Tropical America were to allow the equatorial current to pass through into the Pacific. The effect would at once

be to reduce the temperature of Norway and Britain to that of Greenland and Labrador at present, while the latter countries would themselves become colder. The northern ice, drifting down into the Atlantic, would not, as now, be melted rapidly by the warm water which it meets in the Gulf Stream. Much larger quantities of it would remain undissolved in summer, and thus an accumulation of permanent ice would take place, along the American coast at first, but probably at length even on the European side. This would still further chill the atmosphere, glaciers would be established on all the mountains of temperate Europe and America,* the summer would be kept cold by melting ice and snow, and at length all Eastern America and Europe might become uninhabitable, except by Arctic animals and plants, as far south as perhaps 40° of north latitude. This would be simply a return of the Glacial age. I have assumed only one geographical change; but other and more complete changes of subsidence and elevation might take place, with effects on climate still more decisive; more especially would this be the case if there were a considerable submergence of the land in temperate latitudes.

We may suppose an opposite case. The high plateau of Greenland might subside or be reduced in height, and the openings of Baffin's Bay and the North Atlantic might be closed. At the same time the interior plain of America might be depressed, so that, as we know to have been the case in the Cretaceous period, the warm waters of the Mexican Gulf would circulate as far north as the basins of the present great American lakes. In these circumstances there would be an immense diminution of the sources of floating ice, and a correspondingly vast increase in the surface of warm water. The effects would be to enable a temperate flora to subsist in Greenland, and to bring all the present temperate regions of Europe and America into a condition of subtropical verdure.

It is only necessary to add that we know that vicissitudes not dissimilar from those above sketched have actually occurred in comparatively recent geological times to enable us to perceive that we can dispense with all other causes of change of climate, though admitting that some of them may have occupied a secondary place.‡ This will give us, in dealing with the distribution of life, the great advantage of not being tied up to definite astronomical cycles of glaciation, which may not always suit the geological facts, and of correlating elevation and subsidence of the land with changes of climate affecting living beings. It will, however, be necessary, as Wallace well insists, that we shall hold to that degree of fixity of the continents in their position, notwithstanding the submergences and emergences they have experienced, to which I have already adverted. Sir Charles Lyell, more than forty years ago, published in his "Principles of Geology" two imaginary maps which illustrate the extreme effects of various distribution of land and water. In one all the continental masses are grouped around the equator. In the other they are all placed around the poles, leaving an open equatorial ocean. In the one case the whole of the land and its inhabitants would enjoy a perpetual summer, and scarcely any ice could exist in the sea. In the other the whole of the land would be subjected to an Arctic climate, and it would give off immense quantities of ice to cool the ocean. But Lyell did not suppose that any such distribution as that represented in his maps had actually occurred, though this supposition has been sometimes attributed to him. He merely put what he regarded as an extreme case to illustrate what might occur under conditions less exaggerated. Sir Charles, like other thoughtful geologists, was well aware of the general fixity of the areas of the continents, though

* Abstract.

† Von Wœickoff has very strongly put these principles in a Review of Croll's recent book, "Climate and Cosmology"; *American Journal of Science*, March, 1886.

‡ I may refer here to the admirable expositions of these effects by the late Dr. Carpenter, in his papers on the results of the explorations of the *Challenger*.

* According to Bonney the west coast of Wales is about 12° above the average for its latitude, and if reduced to 12° below the average its mountains would have large glaciers.

‡ More especially the ingenious and elaborate arguments of Croll deserve consideration; and, though I cannot agree with him in his main thesis, I gladly acknowledge the great utility of the work he has done.

with great modifications in the matter of submergence and of land conditions. The union, indeed, of these two great principles of fixity and diversity of the continents lies at the foundation of theoretical geology.

We can now more precisely indicate this than was possible when Lyell produced his "Principles," and can reproduce the conditions of our continents in even the more ancient periods of their history. Some examples may be taken from the history of the American continent, which is more simple in its arrangements than the double continent of Europ-asia. We may select the early Devonian or Erian period, in which the magnificent flora of that age—the earliest certainly known to us—made its appearance. Imagine the whole interior plain of North America submerged, so that the continent is reduced to two strips on the east and west, connected by a belt of Laurentian land on the north. In the great Mediterranean Sea thus produced the tepid water of the equatorial current circulated, and it swarmed with corals, of which we know no less than 150 species, and with other forms of life appropriate to warm seas. On the islands and coasts of this sea was introduced the Erian flora, appearing first in the north, and with that vitality and colonising power of which, as Hooker has well shown, the Scandinavian flora is the best modern type, spreading itself to the south.* A very similar distribution of land and water in the Cretaceous age gave a warm and equable climate in those portions of North America not submerged, and coincided with the appearance of the multitude of broad-leaved trees of modern types introduced in the early and middle Cretaceous, and which prepared the way for the mammalian life of the Eocene. We may take a still later instance from the second continental period of the later Pleistocene or early Modern, when there would seem to have been a partial or entire closure of the North Atlantic against the Arctic ice, and wide extensions seaward of the European and American land, with possibly considerable tracts of land in the vicinity of the Equator, while the Mediterranean and the Gulf of Mexico were deep inland lakes.† The effect of such conditions on the climates of the northern hemisphere must have been prodigious, and their investigation is rendered all the more interesting because it would seem that this continental period of the post-Glacial age was that in which man made his first acquaintance with the coasts of the Atlantic, and possibly made his way across its waters.

We have in America ancient periods of cold as well as of warmth. I have elsewhere referred to the boulder conglomerates of the Huronian, of the Cambrian and Ordovician, of the Millstone-grit period of the Carboniferous and of the early Permian; but would not venture to affirm that either of these periods was comparable in its cold with the later Glacial age, still less with that imaginary age of continental glaciation assumed by certain of the more extreme theorists.‡ These ancient conglomerates were probably produced by floating ice, and this at periods when in areas not very remote temperate floras and faunas could flourish. The glacial periods of our old continent occurred in times when the surface of the submerged land was opened up to the northern currents, drifting over it mud and sand and stones, and rendering nugatory, in so far at least as the bottom of the sea was concerned, the effects of the superficial warm streams. Some of these beds are also peculiar to the eastern margin of the continent, and indicate ice-drift along the Atlantic coast in the same manner as at present, while conditions of greater warmth existed in the interior. Even in the more recent Glacial age, while the mountains were covered with snow and the lowlands submerged

under a sea laden with ice, there were interior tracts in somewhat high latitudes of America in which hardy forest trees and herbaceous plants flourished abundantly; and these were by no means exceptional "interglacial" periods. Thus we can show that while from the remote Huronian period to the Tertiary the American land occupied the same position as at present, and while its changes were merely changes of relative level as compared with the sea, these have so influenced the ocean currents as to cause great vicissitudes of climate.

Without entering on any detailed discussion of that last and greatest Glacial period which is best known to us, and is more immediately connected with the early history of man and the modern animals, it may be proper to make a few general statements bearing on the relative importance of sea-borne and land ice in producing those remarkable phenomena attributable to ice action in this period. In considering this question it must be borne in mind that the greater masses of floating ice are produced at the seaward extremities of land glaciers, and that the heavy field-ice of the Arctic regions is not so much a result of the direct freezing of the surface of the sea as of the accumulation of snow precipitated on the frozen surface. In reasoning on the extent of ice action, and especially of glaciers in the Pleistocene age, it is necessary to keep this fully in view. Now in the formation of glaciers at present—and it would seem also in any conceivable former state of the earth—it is necessary that extensive evaporation should conspire with great condensation of water in the solid form. Such conditions exist in mountainous regions sufficiently near to the sea, as in Greenland, Norway, the Alps, and the Himalayas; but they do not exist in low Arctic lands like Siberia or Grinnel-land, nor in inland mountains. It follows that land glaciation has narrow limits, and that we cannot assume the possibility of great confluent or continental glaciers covering the interior of wide tracts of land. No imaginable increase of cold could render this possible, inasmuch as there could not be a sufficient influx of vapour to produce the necessary condensation, and the greater the cold the less would be the evaporation. On the other hand, any increase of heat would be felt more rapidly in the thawing and evaporation of land ice and snow than on the surface of the sea.

Applying these very simple geographical truths to the North Atlantic continents, it is easy to perceive that no amount of refrigeration could produce a continental glacier, because there could not be sufficient evaporation and precipitation to afford the necessary snow in the interior. The case of Greenland is often referred to, but this is the case of a high mass of cold land with sea, mostly open, on both sides of it, giving therefore the conditions most favourable to precipitation of snow. If Greenland were less elevated, or if there were dry plains around it, the case would be quite different, as Nares has well shown by his observations on the summer verdure of Grinnel-land, which, in the immediate vicinity of North Greenland, presents very different conditions as to glaciation and climate.* If the plains were submerged, and the Arctic currents allowed free access to the interior of the continent of America, it is conceivable that the mountainous regions remaining out of water would be covered with snow and ice, and there is the best evidence that this actually occurred in the Glacial period; but with the plains out of water this would be impossible. We see evidence of this at the present day in the fact that in unusually cold winters the great precipitation of snow takes place south of Canada, leaving the north comparatively bare, while as the temperature becomes milder the area of snow-deposit moves farther to the north. Thus a greater extension of the Atlantic, and especially of its cold ice-laden Arctic currents, becomes the most potent cause of a Glacial age.

I have long maintained these conclusions on general

* As I have elsewhere endeavoured to show ("Report on Silurian and Devonian Plants of Canada"), a warm climate in the Arctic region seems to have afforded the necessary conditions for the great colonising floras of all geological periods. Gray had previously illustrated the same fact in the case of the more modern floras.

† Dawkins, *Popular Science Monthly*, 1873.
‡ "Notes on Post-Pliocene of Canada," Hicks, "Pre-Cambrian Glaciers," *Geol. Mag.*, 1880.

* These views have been admirably illustrated by Von Wæickoff in the paper already referred to, and in previous geographical papers.

geographical grounds, as well as on the evidence afforded by the Pleistocene deposits of Canada; and in an address the theme of which is the ocean I may be excused for continuing to regard the supposed terminal moraines of great continental glaciers as nothing but the southern limit of the ice-drift of a period of submergence. In such a period the southern margin of an ice-laden sea where its floe-ice and bergs grounded, or where its ice was rapidly melted by warmer water, and where consequently its burden of boulders and other *débris* was deposited, would necessarily present the aspect of a moraine, which by the long continuance of such conditions might assume gigantic dimensions. Let it be observed, however, that I fully admit the evidence of the great extension of local glaciers in the Pleistocene age, and especially in the times of partial submergence of the land.

I am quite aware that it has been held by many able American geologists* that in North America a continental glacier extended in temperate latitudes from sea to sea, or at least from the Atlantic to the Rocky Mountains, and that this glacier must, in many places, have exceeded a mile in thickness. The reasons above stated appear, however, sufficient to compel us to seek for some other explanation of the observed facts, however difficult this may at first sight appear. With a depression such as we know to have existed, admitting the Arctic currents along the St. Lawrence Valley, through gaps in the Laurentian watershed, and down the great plains between the Laurentian areas and the Rocky Mountains, we can easily understand the covering of the hills of Eastern Canada and New England with ice and snow, and a similar covering of the mountains of the west coast. The sea also in this case might be ice laden and boulder bearing as far south as 40°, while there might still be low islands far to the north on which vegetation and animals continued to exist. We should thus have the conditions necessary to explain all the anomalies of the glacial deposits. Even the glaciation of high mountains south of the St. Lawrence Valley would then become explicable by the grounding of floe-ice on the tops of these mountains when reefs in the sea. In like manner we can understand how on the isolated trappean hill of Beloeil, in the St. Lawrence Valley, Laurentian boulders far removed from their native seats to the north are perched at a height of about 1200 feet on a narrow peak where no glacier could possibly have left them. The so-called moraine, traceable from the great Missouri Coteau in the west, to the coasts of New Jersey, would thus become the mark of the western and southern limit of the subsidence, or of the line along which the cold currents bearing ice were abruptly cut off by warm surface waters. I am glad to find that these considerations are beginning to have weight with European geologists in their explanation of the glacial drift of the great plains of Northern Europe.

Whatever difficulties may attend such a supposition, they are small compared with those attendant on the belief of a continental glacier, moving without the aid of gravity, and depending for its material on the precipitation taking place on the interior plains of a great continent.

With reference to the transmission of living beings across the Atlantic, we have before us the remarkable fact that from the Cambrian age onwards there were on the two sides of the ocean many species of invertebrate animals which were either identical or so closely allied as to be possibly varietal forms.† In like manner the early plants of the Upper Silurian, Devonian, and Carboniferous present many identical species; but this identity becomes less marked in the vegetation of the more modern times.

In so far as plants are concerned, it is to be observed

that the early forests were largely composed of cryptogamous plants, and the spores of these in modern times have proved capable of transmission for great distances. In considering this we cannot fail to conclude that the union of simple cryptogamous fructification with arboreal stems of high complexity, so well illustrated by Dr. Williamson, had a direct relation to the necessity for a rapid and wide distribution of these ancient trees. It seems also certain that some spores, as, for example, those of the Rhizocarps,* a type of vegetation abundant in the Palæozoic, and certain kinds of seeds, as those named *Ætheotesta* and *Pachytheca*, were fitted for flotation. Farther, the periods of Arctic warmth permitted the passage around the northern belt of many temperate species of plants, just as now happens with the Arctic flora; and when these were dispersed by colder periods they marched southward along both sides of the sea on the mountain chains.

The same remark applies to northern forms of marine invertebrates, which are much more widely distributed in longitude than those further south. The late Mr. Gwyn Jeffreys, in one of his latest communications to this Association, stated that 54 per cent of the shallow-water mollusks of New England and Canada are also European, and of the deep sea forms 30 out of 35; these last of course enjoying greater facilities for migration than those which have to travel slowly along the shallows of the coasts in order to cross the ocean and settle themselves on both sides. Many of these animals, like the common mussel and sand clam, are old settlers which came over in the Pleistocene period, or even earlier. Others, like the common periwinkle, seem to have been slowly extending themselves in modern times, perhaps even by the agency of man. The older immigrants may possibly have taken advantage of lines of coast now submerged, or of warm periods, when they could creep around by the Arctic shores. Mr. Herbert Carpenter and other naturalists employed on the *Challenger* collections have made similar statements respecting other marine invertebrates, as, for instance, the Echinoderms, of which the deep sea crinoids present many common species, and my own collections prove that many of the shallow water forms are common. Dall and Whiteaves† have shown that some mollusks and Echinoderms are common even to the Atlantic and Pacific coasts of North America; a remarkable fact, testifying at once to the fixity of these species and to the manner in which they have been able to take advantage of geographical changes. Some of the species of whelks common to the Gulf of St. Lawrence and the Pacific are animals which have no special locomotive powers even when young, but they are northern forms not proceeding far south, so that they may have passed through the Arctic seas. In this connection it is well to remark that many species of animals have powers of locomotion in youth which they lose when adult, and that others may have special means of transit. I once found at Gaspé a specimen of the Pacific species of *Coronula*, or whale barnacle, the *C. reginæ* of Darwin, attached to a whale taken in the Gulf of St. Lawrence, and which had probably succeeded in making that passage around the north of America which so many navigators have essayed in vain.

It is to be remarked here that while many plants and marine invertebrates are common to the two sides of the Atlantic, it is different with land animals and especially vertebrates. I do not know that any fossil insects or land snails or millipedes of Europe and America are specifically identical, and of the numerous species of batrachians of the Carboniferous and reptiles of the Mesozoic all seem to be distinct on the two sides. The same appears to be the case with the Tertiary mammals, until in the later stages of that great period we find such Genera as the horse, the camel, and the elephant appearing on the two

* Report of Mr. Carvill Lewis in "Pennsylvania Geological Survey," 1884; also Dana's "Manual."

† See Davidson's "Monographs on Brachiopods"; Etheridge, "Address to Geological Society of London"; Woodward, "Address to Geologists' Association"; also Barrande's "Special Memoirs on the Brachiopods, Cephalopods, &c."; and Hall, "Palæontology of New York"; Billings, "Reports on Canadian Fossils"; and Matthews, "Cambrian of New Brunswick, Trans. R. S. C."

* See paper by the author on Palæozoic Rhizocarps, *Chicago Trans.*, 1886.

† Dall, "Report on Alaska"; Whiteaves, *Trans. R. S. C.*

sides of the Atlantic; but even then the species seem different, except in the case of a few northern forms.

Some of the longer lived mollusks of the Atlantic furnish suggestions which remarkably illustrate the biological aspect of these questions. Our familiar friend the oyster is one of these. The first known oysters appear in the Carboniferous in Belgium and in the United States of America. In the Carboniferous and Permian they are few and small, and they do not culminate till the Cretaceous, in which there are no less than ninety-one so-called species in America alone; but some of the largest known species are found in the Eocene. The oyster, though an inhabitant of shallow water and very limitedly locomotive when young, has survived all the changes since the Carboniferous age, and has spread itself over the whole northern hemisphere.*

I have collected fossil oysters in the Cretaceous clays of the coulées of Western Canada, in the Lias shales of England, in the Eocene and Cretaceous beds of the Alps, of Egypt, of the Red Sea Coast, of Judea, and the heights of Lebanon. Everywhere and in all formations they present forms which are so variable and yet so similar that one might suppose all the so-called species to be mere varieties. Did the oyster originate separately on the two sides of the Atlantic, or did it cross over so promptly that its appearance seems to be identical on the two sides? Are all the oysters of a common ancestry, or did the causes, whatever they were, which introduced the oyster in the Carboniferous act over again in later periods? Who can tell? This is one of the cases where causation and development—the two scientific factors which constitute the basis of what is vaguely called evolution—cannot easily be isolated. I would recommend to those biologists who discuss these questions to addict themselves to the oyster. This familiar mollusk has successfully pursued its course and has overcome all its enemies, from the flat toothed selachians of the Carboniferous to the oyster dredgers of the present day, has varied almost indefinitely, and yet has continued to be an oyster, unless, indeed, it may at certain portions of its career have temporarily assumed the disguise of a *Gryphæa* or an *Exogyra*. The history of such an animal deserves to be traced with care and much curious information respecting it will be found in the report which I have cited.

But in these respects the oyster is merely an example of many forms. Similar considerations apply to all those Pliocene and Pleistocene mollusks which are found in the raised sea-bottoms of Norway and Scotland, on the top of Moel Tryfaen in Wales, and at similar great heights on the hills of America, many of which can be traced back to early Tertiary times, and can be found to have extended themselves over all the seas of the northern hemisphere. They apply in like manner to the ferns, the conifers, and the angiosperms, many of which we can now follow without even specific change to the Eocene and Cretaceous. They all show that the forms of living things are more stable than the lands and seas in which they live. If we were to adopt some of the modern ideas of evolution we might cut the Gordian knot by supposing that, as like causes can produce like effects, these types of life have originated more than once in geological time, and need not be genetically connected with each other. But while evolutionists repudiate such an application of their doctrine, however natural and rational, it would seem that nature still more strongly repudiates it, and will not allow us to assume more than one origin for one species. Thus the great question of geographical distribution remains in all its force, and, by still another of our geological paradoxes, mountains become ephemeral things in comparison with the delicate herbage which covers them, and seas are in their present extent but of yesterday when compared with the minute and feeble organisms that creep on their sands or swim in their waters.

The question remains, Has the Atlantic achieved its destiny and finished its course, or are there other changes

in store for it in the future? The earth's crust is now thicker and stronger than ever before, and its great ribs of crushed and folded rock are more firm and rigid than in any previous period. The stupendous volcanic phenomena manifested in Mesozoic and early Tertiary times along the borders of the Atlantic have apparently died out. These facts are in so far guarantees of permanence. On the other hand, it is known that movements of elevation along with local depression are in progress in the Arctic regions, and a great weight of new sediment is being deposited along the borders of the Atlantic, especially on its western side, and this is not improbably connected with the earthquake shocks and slight movements of depression which have occurred in North America. It is possible that these slow and secular movements may go on uninterruptedly until considerable changes are produced; but it is quite as likely that they may be retarded or reversed.

It is possible, on the other hand, that after the long period of quiescence which has elapsed there may be a new settlement of the ocean-bed, accompanied with foldings of the crust, especially on the western side of the Atlantic, and possibly with renewed volcanic activity on its eastern margin. In either case a long time relatively to our limited human chronology may intervene before the occurrence of any marked change. On the whole the experience of the past would lead us to expect movements and eruptive discharges in the Pacific rather than in the Atlantic area. It is therefore not unlikely that the Atlantic may remain undisturbed, unless secondarily and indirectly, until after the Pacific area shall have attained to a greater degree of quiescence than at present. But this subject is one too much involved in uncertainty to warrant us in following it farther.

In the meantime the Atlantic is to us a practically permanent ocean, varying only in its tides, its currents, and its winds, which science has already reduced to definite laws, so that we can use if we cannot regulate them. It is ours to take advantage of this precious time of quietude, and to extend the blessings of science and of our Christian civilisation from shore to shore until there shall be no more sea, not in the sense of that final drying-up of old ocean to which some physicists look forward, but in the higher sense of its ceasing to be the emblem of unrest and disturbance, and the cause of isolation.

I must now close this address with a short statement of the general objects which I have had in view in directing your attention to the geological development of the Atlantic. We cannot, I think, consider the topics to which I have referred without perceiving that the history of ocean and continent is an example of progressive design, quite as much as that of living beings. Nor can we fail to see that, while in some important directions we have penetrated the great secret of Nature, in reference to the general plan and structure of the earth and its waters, and the changes through which they have passed, we have still very much to learn, and perhaps quite as much to unlearn, and that the future holds out to us and to our successors higher, grander, and clearer conceptions than those to which we have yet attained. The vastness and the might of ocean and the manner in which it cherishes the feeblest and most fragile beings, alike speak to us of Him who holds it in the hollow of His hand, and gave to it of old its boundaries and its laws; but its teaching ascends to a higher tone when we consider its origin and history, and the manner in which it has been made to build up continents and mountain chains, and at the same time to nourish and sustain the teeming life of sea and land.

Sugary Matter derived from Toluene and Named "Saccharine."—E. Ferrand and L. Rouquès.—The authors put on record the facts that this compound traverses the organism without any alteration, and that it has an antiseptic property. Its sweetness is not at similar to cane-sugar as it has been asserted. Its flavour is slightly saline and raw.—*Journ. de Pharm.*

* White, "Report U.S. Geol. Survey," 1882—83.

ON THE METHODS OF CHEMICAL FRACTIONATION.

By WILLIAM CROOKES, F.R.S., V.P.C.S.

It has been suggested that it would interest many present were I to give an account of the chemical operation known as "fractionation." I am the more willing to accede to this suggestion as the reference I made to the method on Thursday last might be considered incomplete without some further description of the process. Broadly speaking the operation consists in fixing upon some chemical reaction in which there is the most likelihood of a difference in the behaviour of the elements under treatment, and performing it in an incomplete manner, so that only a certain fraction of the total bases present is separated: the object being to get part of the material in the insoluble, and the rest in the soluble, state. The operation must take place slowly, so as to allow the affinities—which, by the nature of the case, are almost equally balanced—time to have free play. Let us suppose that two earths are present, almost identical in chemical properties, but differing by an almost imperceptible variation in basicity. Add to the very dilute solution dilute ammonia in such amount that it can only precipitate half the bases present. The dilution must be such that a considerable time elapses before the liquid begins to show turbidity, and several hours will have to elapse before the full effect of the ammonia is complete. On filtering we have the earths divided into two parts, and we can easily imagine that now there is a slight difference in the basic value of the two portions of earth; the portion in solution being, by an almost imperceptible amount, more basic than that which the ammonia has precipitated. This minute difference is made to accumulate by a systematic process until it becomes perceptible by a chemical or physical test.

In most methods of fractionation a rough sort of balance of affinities is arrived at before long, beyond which further separation by the same method is difficult. I have long noticed this action when fractionating with ammonia, with oxalic acid and nitric acids, and with formic acid. One valuable point which renders this fact noteworthy is that the balance of affinities revealed by fractionation is not the same with each process. It was in consequence of the experience gained in these different methods of fractionation that in my paper read before the Royal Society, June 10th last (CHEMICAL NEWS, vol. liv., p. 13), after stating that I had not been able to separate didymium into Dr. Auer's two earths, I said "probably didymium will be found to split up in more than one direction according to the method adopted."

The process adopted must vary according to the bodies under treatment. Fractional crystallisation has yielded new results with didymium in the hands of Dr. Auer von Welsbach; and precipitation with formic acid, with ammonia, or with ammonium oxalate, crystallisation of the oxalates from strong nitric acid, and fusing the nitrates and chlorides, have all given me good results.

Working with the samarskite earths, fractional precipitation with oxalic acid separates first erbia, holmia, and thulia, then terbia, and lastly yttria. This is the only method which is applicable for the separation of small quantities of terbia from yttria.

Fusing the nitrates separates ytterbia, erbia, holmia, and thulia from yttria. It is not so applicable when terbia is present, and is most useful in purifying the gadolinite earths. This process is the only one known for separating ytterbia from yttria.

The formic acid process is best for separating terbia, as terbic formate is difficultly soluble in water, the other formates being easily soluble.

Selection must be made of these methods according to

the mixture of earths under treatment, changing the method as one earth or the other becomes concentrated on one side or thrown out on the other. Each operation must be repeated very many times before even approximate purity is attained. The operations are more analogous to the separation of members of homologous series of hydrocarbons by fractional distillation, than to the separations in mineral chemistry as ordinarily adopted in the laboratory.

When the balance of affinities, of which I spoke above, seems to be established, and the earths appear in the same proportion in the precipitate and the solution, they are thrown down by ammonia, and the precipitated earths are worked up by some other process so as to alter the ratio between them, when the previous operation can be again employed.

Fractional precipitation by ammonia is the process generally adopted, for although in some cases it is not so powerful as other processes it is more generally applicable. There are three different methods of operating. According to one plan one-third the equivalent quantity of ammonia is added; then, after the precipitate has quite settled, it is filtered, to the filtrate one-third more ammonia is added, and the precipitate is again filtered off. The remainder of the bases present are then fully precipitated. In this way the earths are divided into three parts, which I will designate -1, 0, and +1. Each of these lots is then treated as just described, and the thirds are added to the vessel on each side. This plan is rapid in the actual separations, but I think more time is spent in the extra filterings and washings than is saved in the lessened number of operations.

The second plan is one which was proposed by Prof. Stokes, with whom I have frequently discussed the subject of fractionation. I am indebted to him for the following description of his plan:—

Suppose that A and B are the two earths in solution. It seems reasonable to suppose that the tendency at any moment to precipitation is such that the proportion of the number of molecules of A to that of B that go down, is that of $p \times \text{No. of molecules of A in solution}$, to $q \times \text{No. of mols. of B in solution}$, where p and q are constants, the reciprocals of which may be called the affinities of the earths for the acid. The proportion is accordingly supposed to change even during a single precipitation.

The separation is best when the ratio of the number of molecules left in solution to the whole number is—

$$\frac{q x + p y}{x + y} \left(\frac{p^p}{q^q} \right)^{1 \div (q - p)}$$

where x and y are the numbers of molecules of A and B present in solution before precipitation.

When p and q are very nearly equal — *i. e.*, the earths have nearly the same affinity for the acid—this ratio becomes $\frac{1}{e}$, where e is the base of the Napierian logarithms, 2.718. . . . This is much nearer three than two, indicating that nearly two-thirds of the whole should be precipitated. Prof. Stokes therefore proposes the following plan:—

Suppose the filtrate to travel to the right and the precipitate to the left. Taking the contents of any bottle, precipitate $\frac{2}{3}$ rds of the whole, and advance the filtrate 2 places to the right and the precipitate 1 place to the left, and so on. Theoretically this is the best way to operate, and I have carried on several long series with much success by its means. There is, however, a slight disadvantage, in that the precipitate is twice as much as the earth in solution; and as the largest part of the operation is the feeding of the filters, I was obliged to fall back on a plan which, although not theoretically so good, makes up for diminished speed by requiring less manipulation.

The third plan is to add half the equivalent amount of precipitant to the liquid, and, after full settlement, filter. Starting with, say, 1000 grms. in the zero bottle, trans-

* Read before the British Association, Birmingham Meeting, Section B.

fer 500 to bottle -1 and 500 to bottle +1. Then add another 1000 grms to the 0 bottle, and repeat the operations as in the following table:—

NUMBERS OF THE BOTTLES.

	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6
							1000						
A.						500	1000	500					
B.					250	500	500	500	250				
C.				125	250	375	500	375	250	125			
D.			63	125	250	375	375	375	250	125	63		
E.		31	63	156	250	312	375	312	250	156	63	31	
F.	15	31	94	156	234	312	312	312	234	156	94	31	15

After the seventh fractionation the 2000 grms. of earth are spread out amongst 13 bottles in the proportions represented in the bottom line.

The separation of *two* earths by either of these plans is comparatively easy. The precipitation by ammonia depends not directly on the affinities of the earths for the acid, but rather on the excess of affinity of the precipitating ammonia. For if the affinities of the two earths are represented by 100 and 101, and that of ammonia by 150, the affinities on which the precipitation depends would be represented by $150 - 100 = 50$, and $150 - 101 = 49$, the difference of which is 2 per cent of the larger.

Now if a precipitant of which the affinity for the acid was only 110 were used, the affinities in question would be $110 - 100 = 10$, and $110 - 101 = 9$, and the difference, $10 - 9 = 1$, is 10 per cent of the larger instead of only 2 per cent. Therefore if an alkali, for which the affinity of the acid was only a little greater than that of the earths, were used for precipitation, it is likely that the differences between the two earths would come out more strongly, and the labour of fractional precipitation might be much reduced. Prof. Stokes has suggested that some of the compound ammonias might prove useful as precipitants instead of ammonia. I have not, however, tested this suggestion.

In Prof. Stokes's method he assumes that as each portion of precipitate falls of its own accord in the same precipitation, the proportion of the earths in the next small portion is that of the quantities remaining in solution multiplied by their respective inverse affinities. If, however, the proportion depends only on the proportions they had when the ammonia was added, but the precipitation had not yet commenced, so that all the flocks which fall one after the other have the same composition, the result will be different. In this case the best result would be obtained by precipitating one-half. When the precipitation is hurried I think the Stokes plan is best, but when the precipitation is so slow that half an hour or more elapses before even a turbidity is apparent in the liquid, I think all the different parts of the precipitate have the same composition, and my plan may be the best.

The values of the two methods, Prof. Stokes's and mine, may be illustrated thus:—In the Stokes method we have two-thirds sent one step to the right and one-third to the left. The value of a step is 0.795, say 0.8. This gives —two-thirds at 0.8, plus one-third at 1.6 = 1.067. By my method half the quantity is transported one place to the right and half one place to the left. Taking the value of a step as unity the separation is, half at one plus half at one, = 1. The result of this estimate is to make the Stokes method about 7 per cent better than mine. As the value of a step in the Stokes process is only about four-fifths of a step in mine, about a fourth more bottles would be required to effect an equal purification. But, on the other hand, the travelling right or left is very distinctly quicker in the Stokes method than in mine. In going right by his plan we take two steps at a bound, though it is true we carry with us only one-third instead of one-half the quantity. In going left we take one step, but then we carry two-thirds instead of only half with us; and in a second operation on this quantity, only one-

third, instead of one-half, of that which had come to the left would be carried to the right.

Whichever plan is adopted the amount of earths present has to be determined before each precipitation, so as to know how much ammonia is to be added to get the half or two-thirds precipitated. This is done by standard solutions, and when everything is in good order it does not occupy much time. Filtration is always the lion's share of the trouble.

The above calculations have been based on the assumption that only two earths are present. If more than two are present, either of the above processes fails, in any reasonable time, to yield practically pure specimens of more than two out of a group of closely allied earths. Thus if there are as many as three earths, say A, B, and C, whose positions in reference to the chemical process employed are in the order of sequence in which they are written, we may get a specimen of A as nearly as we please free from B and C, and a specimen of C as nearly as we please free from A and B, but we cannot get a specimen of B practically free from A and C. The law seems to be that *to obtain practically pure specimens of three closely allied earths, it is essential to have recourse to at least two different chemical processes.* The mere continued repetition of the same process will not do, unless indeed the operations are repeated such a vast number of times as to make the approximate expressions no longer applicable, even though the substances are chemically very close.

With a greater number of earths the same law holds good; thus with n earths closely allied, to be separated, we must have recourse to $n - 1$ different chemical processes.

I have sometimes adopted the following plan of precipitation:—Having ready standard solutions of acid and ammonia, I add to the neutral solution ammonia sufficient to precipitate nine-tenths of the earths present; after the whole is down I add enough acid to dissolve eight-tenths of the total quantity; then ammonia to precipitate seven-tenths; next acid to dissolve six-tenths, and so on, leaving off when the proportion of precipitate is what is required in the operation. The solutions must be so dilute that no precipitation takes place for some time, and the vessels must be well agitated during the whole operation. This makes the separating value of one operation, involving only one filtration, far greater than that of a simple fractional precipitation. The vessels may be of any size, from that of a few gallons to the tubs and tanks used on a manufacturing scale. In a small laboratory such large vessels, however, become unwieldy, and their agitation becomes difficult. Moreover, the rarity of the material makes it unadvisable to use too large vessels, as the unavoidable loss by transference, and the solution in mother-liquors, is greater in large vessels. After long experimentation I have come to the conclusion that common Winchester quart bottles are the best vessels for the precipitations, using several bottles at first for each single precipitation, until the quantity of earths is reduced to within the capacity of one bottle.

The acid in which the earths are dissolved is not a matter of indifference. There is an objection to sulphuric acid on the ground of its disposition to form double salts, so that of the sulphates in solution a good portion might be double sulphates, in which the two molecules of base combined with one of acid consisted one of one base and one of the other; and the two molecules thus intimately associated might tend to remain together, whether as precipitate or as filtrate. On the whole I prefer nitric acid, as having little tendency to form double salts and being easily got rid of.

It is occasionally necessary to completely precipitate the whole contents of the bottles with ammonium oxalate, and after ignition to re-dissolve the earths in acid, and proceed as before. If this precaution is not adopted the accumulation of ammonium nitrate in the solution dissolves an appreciable amount of the earths.

In the ordinary operations of separating distinct enti-

ties, such as the known gadolinite or samarskite earths, it is not difficult, as I have already pointed out, to find different chemical processes, which may be successively employed. When, however, the separations attempted are those of the constituents of yttrium, simple straightforward fractionation, continued steadily month after month and year after year, is the only plan I know.

The operation may be somewhat hastened by removing from the main series certain bottles in which one particular constituent is concentrated, and sub-fractioning these by themselves. Also, to avoid the spreading out sideways to too great an extent, after a certain distance has been proceeded from the centre, say to bottles -20 and +20, the earths are allowed to accumulate in the last bottle at each end. They will after a time be in sufficient amount to sub-fractionate on their own account, and, being at the end of the series, they offer a good chance of getting the two extreme constituents pretty pure.

It will be seen from the above description that there is little hope of success in fractionation unless the supply of crude earths is very large. In my laboratory I have, either worked up or ready for working, over 50 kilos. of samarskite containing about 10 per cent of yttria, and about 20 kilos. of gadolinite containing 48 per cent of yttria, besides a considerable quantity of other rare yttria minerals, giving a total yield of more than 15 kilos. of yttria.

PREPARATION OF IODALDEHYD.

NOTE ON THE REPLY OF M. P. CHAUTARD.

By W. POPPLEWELL BLOXAM and E. F. HERROUN.

M. CHAUTARD has done us the honour of replying to some remarks and questions of ours which appeared in the *CHEMICAL NEWS* (vol. liii., p. 301) of June last.

We notice that, while M. Chautard repeats his statement that in the preparation of iodaldehyd the reaction is complete in three or four days in summer and eight in the coldest part of the winter, he now informs us that in his experiments the matrass was placed on a staging over a stove where the temperature averaged 30° to 40°, while in his original memoir he distinctly states that the matrass is left at the surrounding temperature. We regret that this misunderstanding as to temperature should have arisen, as, in endeavouring to follow M. Chautard's directions to the letter we did not feel justified in raising the temperature above about 25° at most.

With reference to the question of mass, we gather from M. Chautard's remarks that whilst it is just possible to obtain the iodaldehyd, using only 5 grms. of aldehyd, yet he acknowledges that, working under conditions analogous to those we have employed (*viz.*, those he himself lays down in his original paper), he had much trouble in getting "any results."

We therefore think our criticism of M. Chautard's method as then published was justifiable, and we await with interest the publication which he proposes to make shortly of his modifications and new methods.

We introduced, among others, the quotation from Schoonbroodt to which M. Chautard refers to illustrate the unsatisfactory condition of the present knowledge of the subject rather than to indorse any opinions there expressed, and from our own experience we are quite prepared to believe that the solid product obtained by him was simply a mixture of iodoform and potassic iodide, as M. Chautard now informs us. We are pleased to see that M. Chautard is engaged in elucidating the nature of the decomposition of mon-iodaldehyd by alkalies, yielding iodoform, as it appears to us a point of considerable importance in establishing the position of mon-iodaldehyd among substitution-products.

We further note with interest that M. Chautard has

succeeded in obtaining a number of iodo substitution-products of aldehyds of the fatty series. We would take this opportunity of expressing our opinion of the great debt our science will owe to M. Chautard for investigating a subject of so much importance, but obscure and attended by so much experimental difficulty and discomfort.

THE SANITARY VALUE OF THE CHEMICAL ANALYSIS OF POTABLE WATERS.*

By WILLIS G. TUCKER, PH.D.

(Concluded from p. 102.)

THESE, then, are the principal methods, and the best at present known for the determination of organic matter in potable water.† It will be seen that no one of them enables us to recognise the real morbid material which water may contain or is able to distinguish with certainty between disease-producing constituents and the less harmful or innocent matter of vegetable origin, or that which has resulted from the conversion of harmful into harmless substances. The English Society of Public Analysts have adopted a scheme of analysis which includes both the permanganate and albumenoid ammonia processes, and this method has been largely followed in this country and adopted by our State Board of Health. I have employed it in quite a large number of cases, and it has frequently happened that waters, which had in all probability caused disease, could not be condemned on the evidence furnished by the analysis alone. Mallet would use "all three of the principal processes," since "each gives a certain amount of information which the others do not afford," and adds that "under circumstances admitting only of the use of simpler means of investigation, the albumenoid ammonia and permanganate processes might be employed together, but in no case should only one of these methods be resorted to, such a course entailing practically the neglect of carbon on the one hand or nitrogen on the other." This opinion is based upon the results of an extended research, and to admit that the determination of carbon and nitrogen—perfectly harmless elements in themselves—affords us our best indications in judging of the purity or impurity of a water is to acknowledge that our best analytical methods are far from satisfactory.

What, then, are the questions which a chemical analysis can answer concerning a water viewed from a hygienic standpoint? It may be answered, first, that all attempts to establish definite standards, so that the points for and against a water can be counted up and a balance struck, have signally failed. For there is no unanimity of opinion as to what degree of importance should be attached to the results obtained, and, if there was, such a numerical expression of their relative importance must of necessity be arbitrary and misleading. A committee of the German Public Health Association reported to this effect at the Dusseldorf Meeting in 1883, and the opinion of this committee accords with that of most sanitarians who have investigated the subject.

Secondly, it may be said that with the various means at present at our command, waters which are very pure, chemically, of medium purity, and foul, may be distinguished, but whether these waters are therefore safe to use, doubtful, or harmful, must be a matter of opinion, and is not to be decided by the analytical results. You may take a few spoonfuls of the dejection of a typhoid fever patient and add them to a barrel of distilled water,

* A Paper read before the Albany Institute.

† The scope and limits of this paper do not admit of a consideration of certain recently proposed analytical processes like the "actinic method," in which silver salts in solution are reduced by organic matter when exposed to sunlight, nor of indirect methods of analysis like the determination of the gaseous constituents to which reference has been made.

and a chemical analysis will tell us that the water is pure, and you may add a pound of healthy faecal matter to another barrel of distilled water, and an analysis will show that it is defiled; yet the first water may, if drunk, give rise to typhoid fever, and the second to no harmful results at all. The analysis of water is like that of air. It can show us the relative amounts of the main and gross constituents, but the organised and living material which may be present, and if so is probably most instrumental in producing disease, can be neither recognised as such nor measured. In the appendix to the report of the Medical Officer of the Local Government Board of Great Britain for 1881, is a report by Dr. Cory on the chemical examination of certain samples of water purposely polluted with excrements from enteric fever patients and other matters. Dr. Buchanan sums up the result of the inquiry by saying: "While we must ever be on the watch for the indications that chemistry affords of contaminating matters gaining access to our waters, we must (at any rate until other methods of recognition are discovered) go beyond the laboratory for evidence of any drinking water being free from dangerous organic pollution. Unless the chemist is well acquainted with the origin and liabilities of the water he is examining he is not justified in speaking of a water as "safe" or "wholesome" if it contains any trace of organic matter whatever; hardly, indeed, even if it contains absolutely none of such matter appreciable by his very delicate methods. The chemist can, indeed, tell us of impurity and hazard, but not of purity and safety. For information about these we must go, with what the chemist has been able to teach us, in search of the conditions surrounding water sources and affecting water services."

We are not, therefore, to infer that water analysis is useless because, in the present state of our knowledge, there are many questions which it cannot satisfactorily answer, for an analysis of a water may reveal to us the presence of compounds which have doubtless resulted from the decomposition of animal matter, as, for instance, in showing us that a well is contaminated by leakage from a cess-pool or privy, or that a reservoir, pond, or river is defiled by sewage matter. Now in the first case the pollution of the well may be harmless, but in the event of specific polluting material entering at any time, as it is quite likely to do at some time, such a well may become a centre for spreading disease, and if so its water should not be used at all, and in the other case, if a larger body of water is markedly polluted by sewage, while the certainty of proving unwholesome or producing specific diseases may not be provable, we shall err on the safe side if we refuse to use such water, the chemical evidence being considered, at least, until we can cut off the access of contaminating matter.

And lastly an analysis may assure us that a given water is of such a degree of purity that the probabilities are that it carries with it no harmful matter, but this kind of evidence is always to be received with caution unless the results of the examination are borne out by other evidence which proves that pollution is not probable. Thus, while a chemical analysis alone cannot tell us that a water is absolutely safe or necessarily harmful, it *can* tell us that a water contains those constituents which may reasonably be believed to accompany harmful matter, and if the question be as to the employment of a given water for a city supply, an exhaustive series of analyses made at different points, stages, times, and seasons may reveal to us the degree of pollution, points at which the polluting matter enters, rapidity of its destruction by natural processes, and the conditions of the water under varying circumstances, and also indicate to us the methods to be employed for improving its quality and obtaining it at its best estate. Such series of analyses have been made during late years in our own country by various chemists, and with very satisfactory results. But a single analysis, or a few analyses, may give us little information or be entirely misleading.

Previous reference has been made to the investigations of Professor Mallet, and as no more thorough work has ever been done in this direction, at home or abroad, and as the conclusions arrived at as the result of an exhaustive study of a multitude of facts confirm the opinions just expressed, some of these conclusions from his report are quoted:—

"1. It is not possible to decide absolutely upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of the processes examined for the estimation of organic matter or its constituents."

"2. I would even go further and say that in judging the sanitary character of a water, not only must such processes be used in conjunction with the investigation of other evidence of a more general sort as to the source and history of the water, but should even be deemed of secondary importance in weighing the reasons for accepting or rejecting a water not manifestly unfit for drinking on other grounds."

"3. There are no sound grounds on which to establish such general "standards of purity" as have been proposed, looking to exact amounts of organic carbon or nitrogen, "albumenoid ammonia," oxygen of permanganate consumed, &c., as permissible or not."

"4. Two entirely legitimate directions seem to be open for the useful examination by chemical means of the organic constituents of drinking water, namely:—First, the detection of *very gross* pollution, . . . and secondly, the periodical examination of a water-supply, as of a great city, in order that the normal or usual character of the water having been previously ascertained, any suspicious changes which from time to time may occur shall be promptly detected and their cause investigated."

It was proposed only to discuss chemical methods of examination in this paper, and therefore no reference has been made to the microscopical examination of water deposits, or to biological investigations. The former are often of value and from the latter it was at one time thought, and this is still the opinion of many, that almost everything might be learned, and that chemical analysis had had its day, and was destined to be entirely replaced by biological investigations. Whether the results obtained so far have justified this view is certainly an open question. In my opinion they have not. That such investigations should be made in connection with chemical analyses is generally conceded, and doubtless when our knowledge has increased very valuable results may be obtained thereby, for the probable significance of some classes of micro-organisms seems to be established; but as Mallet has pointed out, basing his statement upon work done by Professor H. Newell Martin, of the Johns Hopkins University, Dr. George M. Sternberg, U.S.A., and others, there is the difficulty often presented "either by the sparseness, or more frequently the abundance, of those organisms in fairly estimating their average relation to the mass of water," and "this difficulty is superadded, of course, to the imperfection of our knowledge as to the effects upon human health of some closely allied—even hardly distinguishable—organisms of dangerous and harmless associations, and of perhaps the same organism in different stages of its life-history."

Two other subjects proposed for discussion remain to be briefly considered. And first as regards the dissemination of diseases by drinking water, there is so much evidence to support the view that polluted waters are prolific sources of disease, that to deny such a cause as an important factor in the propagation of many zymotic diseases, is, to say the least, illogical. Countless sporadic cases of typhoid fever, for instance, have been traced to the use of drinking water polluted by the dejections of those suffering with this disease, and many epidemics of typhoid and cholera have been clearly shown to have had a similar origin. I cannot refrain, in this connection, from referring to the history of the cholera epidemics in Glasgow and Manchester during the present century, taking the facts

from the Rivers Pollution Commission Report for 1874. Up to 1859 Glasgow drew its water supply from the Clyde, which was polluted by the drainage of towns higher up the river. After that year a pure supply was obtained from Loch Katrine. The deaths from cholera in 1832 were 2842; in 1849, 3772; in 1854, 3886; and in 1866, 16; Manchester and Salford have a similar history. Up to 1851 they took their water partly from the River Irwell and partly from wells, both sources being much polluted. In 1832 there were 890 deaths from cholera; in 1849, 1115; and after the introduction of pure water in the epidemic of 1854, but 50 cases, and in 1866, 88 cases. It will be observed that, in the general epidemic of 1854, Glasgow, using polluted water from the Clyde, had 3886 deaths from cholera, while Manchester and Salford, with a purer supply, had but 50 deaths. The death rate per thousand per annum of Manchester, previous to the introduction of its present water supply, was 33, while in 1880 it was 24.7. (Usill, "Statistics of the Water Supply of the Principal Cities and Towns of Great Britain and Ireland," 1881). In 1832 there were 1000 deaths from cholera in Exeter, England, but after purer water was supplied from a point two miles higher up the river than before, and above the point at which the sewage of the town entered; when cholera again visited the city, in 1849, there were but 44 cases, and in 1854 hardly a single case occurred. In 1854 the water supplied by the Southwark Company, in London, was polluted by sewage, while that of the Lambeth Company was much purer. These companies had pipes in the same streets, and supplied consumers indiscriminately on both sides of streets. The deaths from cholera among those who used the Southwark water were 130 in 10,000, while they were but 37 in 10,000 among those using the better water of the Lambeth Company, while in 1849, when that company took water from a point lower down the river than the Southwark, the death rate was largest among those using their water.

Dr. John Simon, Chief Medical Officer of the Privy Council and of the Local Government Board of Great Britain, testified as follows before the Rivers Pollution Commission: "It is, I think, a matter of absolute demonstration that in the old epidemics, when the south side of London suffered so dreadfully from cholera the great cause of the immense mortality there was a badness of the water supply then distributed in those districts of London."

In all this nothing has been said about disease germs, for like the chemist's atoms their existence even is not proved, though it seems certain that many diseases are produced by specific poisons, of the nature of which we as yet know little, and that in certain diseases these poisons are contained in the excreta, which may give rise to these same diseases through the use of drinking water to which they have gained access. All filth is not necessarily harmful, a statement which hardly needs proof, but the truth of which is well seen in the case reported by Dr. J. C. McKee, U.S.A., in the *New York Medical Journal* for November 3, 1883, in which water containing large quantities of putrescent animal matter was used for two weeks by a garrison of eighty people, including men, women, and children, without producing any deleterious effects, but if some specific kinds of filth are poisonous, then the use of a given water which is liable at any time to become specifically polluted should be abandoned, if possible, in favour of a safer source of supply.

And lastly, as regards the natural purification of polluted waters, while the tendency of all organic matter, animal or vegetable, is toward ultimate death and final destruction by oxidation, it is as yet impossible to say how rapidly such a destruction goes on in many cases. The Rivers Pollution Commission mixed urine with water, in the proportion of one part of urine to 3077 of water, agitated the mixture from time to time, and analysed samples. At the end of the eleventh day the improvement in the water was so inconsiderable that other experiments were made in which a stream of impure water was allowed to flow from

one vessel to another, and was thus freely exposed to the air, and as a result of these experiments the commissioners concluded that purification by natural oxidation had been greatly over-rated, and that "there is no river in the united kingdom long enough to secure the oxidation and destruction of any sewage which may be discharged into it even at its source." They also conclude that "rivers which have received sewage, even if that sewage has been purified before its discharge, are not safe sources of potable water." (Rivers Pollution Commissioners' 6th Report, pp. 134-8.) Upon this point Frankland says:—"Twelve years ago there was a general impression amongst chemists and others that polluted water quickly regained its original purity by spontaneous oxidation. The opinion had no foundation in quantitative observations; indeed there was not a single experimented fact to prove it. . . . The impression had gained currency from the improved appearance of a polluted river after a flow of a few miles. . . . Two classes of persons strongly interested in its acceptance were chiefly instrumental in the origination and diffusion of this opinion. These were, first, the polluters of running water, and, secondly, water companies drawing their supplies from below the sewer outfalls of towns." (*Journal Chemical Society*, May and July, 1880.) Such improvement as does take place in running streams probably depends more upon the part played by fresh-water plants and micro-organisms than upon direct chemical oxidation, and of course no accurate conclusions can be reached as to the effect of these varying and little understood agencies. Mere dilution also doubtless accounts for the apparent disappearance of much noxious matter. Professor Wm. Ripley Nichols, in his *Water Supply*, italicises the following statement:—"The apparent self-purification of running streams is largely due to dilution, and the fact that a river seems to have purified itself at a certain distance below a point where it was certainly polluted, is no guaranty that the water is fit for domestic use."

To what extent, therefore, must a polluted water be diluted before it is safe to use, is a question of the greatest interest, but one to which no answer can as yet be given. Nor can we prove that the specific poisons of certain diseases—admitting their existence—may not contain living organisms capable of rapid multiplication, nor can we tell for how long a period or under what conditions these organisms may retain their vitality. In this absence of positive knowledge, but in the light of countless facts which all but prove our suppositions true, we had best err, if err we must, on the safe side, avoiding the use of polluted waters and recognising the fact that although chemical analysis may detect no impurities in a water, it is not, therefore, necessarily safe to drink.

The views here presented may seem extreme to those who have long believed on insufficient grounds that from a chemical analysis alone the character of a drinking water may be decided. My endeavour has been to deal with facts, and make no claims for the chemist's ability in this direction which may not be substantiated, and until we have more knowledge than we now possess of the real causes of disease, and until other methods of analytical research shall have been discovered, it is futile to ask the chemist to recognise and measure forms of matter of which he is ignorant, and to state what will be the effect upon the human system of substances the very nature of which is as yet to him unknown.

Gas Engines.—The Government have ordered four 4-horse power "differential" gas engines, Atkinson's patent, with patent air-compressors combined, to work in connection with "Shone's" system of pneumatic drainage, which is being applied to the Houses of Parliament for dealing with the sewage. The engines are to be fixed in the basement under the chambers.

COMMUNICATIONS ON GERMANIUM.

By CLEMENS WINKLER.

For the extraction of germanium argyrodite is smelted with an equal weight of a mixture of equal parts of soda-ash and flowers of sulphur. The solution obtained by lixiviating the melt is mixed with a quantity of sulphuric acid sufficient for neutralisation, whereby sulphur and antimony and arsenic sulphides are precipitated. From the filtrate germanium sulphide is thrown down by the addition of more acid and washed with dilute acid containing hydrogen sulphide. On heating the sulphide with strong nitric acid or driving off the sulphuric acid from the washed sulphide germanium oxide is obtained and may be reduced at a red heat in a current of hydrogen. For the reduction of large quantities it is preferable to knead up the oxide with 10 to 15 per cent of starch and boiling water and ignite moderately in a covered crucible. Germanium is thus obtained as a dark-grey powder. It melts to a very fluid regulus under a layer of borax glass, its melting-point being about 900° . It has a great tendency to regular crystallisation. It is very brittle, easily pulverised, and has a distinct conchoidal fracture. Germanium has a fine metallic lustre, a greyish white colour, and its sp. gr. is 5.469. It is not soluble in hydrochloric acid, but readily in *aqua regia*. Nitric acid converts it into a white oxide, and, on heating with strong sulphuric acid, SO_2 is given off and a white soluble sulphate is formed. Potassa lye has no action. With nitrates and chlorates it yields deflagrating mixtures. The atomic weight was determined by titrating the chlorine contained in the tetrachloride, according to Volhard's method, and found = 72.32. The value obtained by Lecoq de Boisbaudran by a totally different process is 72.28.

The vapour density of the tetrachloride has been determined by L. F. Nilson and O. Petterson, of Stockholm, as 7.43 at 301.5° , and 7.44 at 739° . G. Kobb, of Stockholm, has studied the spark spectrum of germanium. He found as particularly distinct and capable of measurement a line in the orange, one in the yellow, four in the violet, and twelve in the green and the blue.

The compounds of germanium certainly known are two oxides, two sulphides, two chlorides, and one iodide. Many germanium compounds are distinguished by their solubility and some by their volatility. In the flame of the Bunsen burner they give neither a colour nor a spectral reaction. These solutions are slowly precipitated by various metals which decompose water, especially zinc, free germanium being deposited. Most germanium compounds are readily decomposed at elevated temperatures by reducing agents.

Oxides of Germanium.—Compact germanium retains its lustre in the air, but becomes coated with a thin layer of oxide at a red heat. Pulverulent germanium, obtained by reduction, burns like tinder at a gentle heat. Strong nitric acid also effects its oxidation. Germanious oxide, GeO , is obtained on decomposing the chloride, GeCl_2 , by means of an alkali. The first product is germanious hydroxide, which, on gently heating in a current of carbonic acid, yields the blackish grey oxide, GeO . It is insoluble in dilute sulphuric acid, but dissolves readily in hydrochloric acid. The solution gives a characteristic reaction and is a powerful reducing agent. It converts chromic acid into chromium sesquioxide, &c., and bleaches litmus instantaneously. It has not been ascertained if germanious oxide is capable of forming oxy-salts.

Germanic oxide (germanious acid?), GeO_2 , is formed on burning the element in oxygen, on oxidising by means of nitric acid, or on roasting the sulphides. It is obtained perfectly pure by decomposing the chloride with water. Germanic oxide is a dense white powder, sp. gr. 4.703, perfectly permanent on ignition. At 20° 1 part of the oxide dissolves in 247.1 parts of water, and, at 100° , 95.3 parts. On evaporating the solution microscopic crystals

are formed. At a moderate red heat this oxide is reduced to germanium by hydrogen or charcoal. It is sparingly soluble in acids, though oxy-salts appear to exist. Its true character is that of an acid, which is confirmed by its solubility in alkalies.

Germanious sulphide, GeS , is formed by heating germanic sulphide, along with an excess of germanium, in a current of carbonic acid or in a slow current of hydrogen. Close beyond the heated spot there are formed thin tables or plumose crystals, grey by reflected but red or orange by transmitted light. If this sulphide is heated in the air it becomes an oxide. It is readily soluble in potassa-lye. From the solution hydrochloric acid throws down amorphous germanious sulphide as an orange powder, which dissolves to chloride in hot strong hydrochloric acid. Amorphous germanious sulphide (though not the crystalline form) dissolves in ammonium sulphide.

Germanic sulphide, GeS_2 , is best obtained by precipitating a solution of the oxide with hydrogen sulphide. The voluminous white precipitate is first washed with dilute acid, saturated with H_2S , the acid is then expelled by means of alcohol, saturated with sulphuretted hydrogen, and the washing is then completed with ether, and the product dried in a vacuum. The sulphide is moderately soluble in water. When dry it undergoes spontaneous decomposition in moist air. It is a sulpho-acid and argyrodite is its natural sulpho-salt. Alkaline sulphides form with it soluble sulpho-salts, which seem to precipitate insoluble sulpho-germanates from the solutions of the heavy metals.

Chlorides of Germanium.—Compact germanium ignites when heated in chlorine and burns with a bluish-white flame to vapours of the tetrachloride. Germanium in the state of powder ignites spontaneously in chlorine.

Germanious chloride, GeCl_2 , is obtained by passing hydrochloric gas over powdered germanium. It is a colourless limpid fuming liquid; its vapour turns cork an intense red. The liquid boils at 72° , which leads to the suspicion that we have here not the dichloride, but possibly a compound, GeHCl_3 , analogous to silicon-chloroform. The addition of a little water separates from the above compound a dense white precipitate, probably an oxychloride. The hydrochloric solution of germanious chloride is a powerful bleaching and reducing agent.

Germanic chloride, GeCl_4 , is formed by the direct contact of its elements and is freed from free chlorine by contact with mercury. It is a colourless liquid of sp. gr. 1.887 at 18° . It boils at 86° , does not congeal at -20° , fumes in the air, and is decomposed by water.

The iodide, GeI_4 , is obtained by the direct contact of its elements. It is of an orange colour, turning yellow if pulverised; melts at 144° and seems to boil between 350° and 400° . It is very hygroscopic, and on contact with water it is gradually converted into white oxide.

A characteristic reaction for germanium has not yet been discovered. The best means for its recognition is the formation of the white sulphide on the addition of ammonium sulphide to an alkaline solution of germanium, followed by a copious addition of hydrochloric acid. This sulphide is the only form into which germanium can be converted for quantitative determination. As germanium forms sulphides soluble in alkaline sulphides it takes place analytically along with arsenic, antimony, and tin. —*Chemiker Zeitung*.

Inversion of Cane-Sugar by Benzoic Acid and the Oxybenzoic Acids.—M. Koral.—From the author's researches it appears that the results on the affinity of the four acids (benzoic, salicylic, meta-oxybenzoic, and para-oxybenzoic) obtained by Prof. Ostwald by means of their electrolytic conductivity agree with the results obtained by the speed of inversion of cane-sugar, and are thus confirmed.—*Fourn. Prakt. Chem.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 7, August 16, 1886.

Mono-substituted Haloid Derivatives of Acetonitrile.—Louis Henry.—The author concludes that the proximity of nitrogen and of the halogen bodies in carbon compounds communicates to them special properties. This proximity exerts upon the entire molecule volatilising action. It gives the carbon compounds the power of acting strongly upon the skin and the moist mucous membranes. Lastly, it augments the aptitude of reacting upon positive elements. In this three-fold respect nitrogen plays a part similar to that of oxygen.

Composition of the Waters of Bagnères de Luchon.—Ed. Willm.—A paper of no direct chemical interest. None of the rare elements have been detected in the water.

Journal de Pharmacie et de Chimie.
Vol. xiv., No. 3, August 1, 1886.

Action of an Electric Current upon Anhydrous Hydrofluoric Acid.—H. Moissan.—This paper, here inserted among "Travaux Originaux," appeared in the *Comptes Rendus* (vol. cii., p. 1543), and thence in the *CHEMICAL NEWS* (vol. liv., p. 36).

Researches on Ramie.—E. Fremy.—Already noticed.

The Seeds of Bonduc, and their Active Febrifuge Principle.—E. Heckel and F. Schlagdenhauffen.—These seeds are produced by two Brazilian plants, *Casalpinia Bonducella* and *C. Bonduc*. The active principle is non-nitrogenous, and its composition is expressed by the formula $C_{14}H_{15}O_5$.

The Synthesis of an Inactive Terpinol.—G. Bouchardat and J. Lafont.—Already noticed.

Chemical Composition of Japanese Drops.—M. Hupier.—These drops consist of menithol.

Officinal Cinchona Bark.—G. Vulpius.—From the *Chemiker Zeitung*.

Assay of Cocaine.—Cocaine may be modified by the presence of hygrine and ecgonine. If on treating cocaine hydrochlorate with strong sulphuric acid in the cold, we obtain a perfectly colourless solution, the sample is perfectly pure; if the solution is coloured the above-named alkaloids are present.

Journal für Praktische Chemie.
New Series, Vol. xxxiv., Part 2.

Action of Orthotoluidine upon Hydroquinone and Resorcin.—M. Philip.—If hydroquinone is heated with orthotoluidine and calcium chloride, or with orthotoluidine alone, there is formed a mixture, varying according to circumstances, of para-oxyphenyl-orthotolylamine and of diorthotolyl-para-phenylen-diamine. The yield of the former base is from 30 to 50 per cent of the theoretical quantity. The derivatives obtained were the hydrochlorate, the dimethyl-ether, and the formyl-, diacetyl-, and dibenzoyl-compounds. Diorthotolyl-para-phenylen-diamine forms white, shining leaflets, melting at 135° , and distilling undecomposed at 420° in a current of hydrogen. Its sulphuric solution is turned of a characteristic violet-blue colour by nitric acid. The yield of diamine was about 80 per cent of the possible quantity. Of the derivatives of resorcin only meta-oxyphenyl-orthotolylamine was obtained in a state of approximate purity.

Investigations on the Relations of Equilibrium in Aqueous Solutions. Part II.—Existence of Acid Salts and Double Salts in Aqueous Solutions.—Acid sodium tartrate is completely resolved into normal salt and free acid only if infinitely diluted, whilst the solution, as its concentration increases, contains larger and larger quantities of the acid salt. The acid alkaline malates are also decomposed by water, but only in part, as complete decomposition would be effected only in infinite dilution. It is probable that double potassium-sodium tartrate is completely resolved into the two single salts, even in strong aqueous solutions.

Action of Chlorine and Bromine upon Organic Bromides and Iodides.—R. Meyer.—This paper does not admit of useful abstraction.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Birmingham Meeting of the British Association:—

President.—William Crookes, F.R.S.

Vice-Presidents.—Prof. Thomas Carnelley, D.Sc.; Dr. W. H. Perkins, V.-P.C.S.; Prof. H. E. Armstrong, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. G. Vernon-Harcourt, LL.D., F.R.S.; Dr. W. J. Russell, F.R.S.; Prof. W. A. Tilden, D.Sc., F.R.S.; Prof. A. W. Williamson, Ph.D., LL.D., F.R.S.

Secretaries.—Prof. P. Phillips Bedson, D.Sc. (Recorder); H. B. Dixon, M.A., F.R.S.; H. Forster Morley, M.A., D.Sc.; W. W. J. Nicol, M.A., D.Sc.; C. J. Woodward, B.Sc.

Committee.—A. H. Allen; C. H. Bothamley; H. B. Brady, F.R.S.; A. M. Chance; Sir John Conroy, M.A.; J. T. Dunn, M.Sc.; H. Emmons; T. Fairley; Alfred E. Fletcher; Prof. W. N. Hartley, F.R.S.; C. W. Heaton; E. H. Horne; Prof. Herbert McLeod, F.R.S.; Prof. R. Meldola, F.R.S.; H. R. Mill, D.Sc.; D. H. Nagel; F. G. Newbolt; Prof. W. Ramsay, Ph.D.; W. Chandler Roberts-Austen, F.R.S.; W. T. Ryland; C. Meymott Tidy, M.D.; W. Thorp; Thomas Turner; George Ward; R. Warrington, F.R.S.; W. Marshall Watts, D.Sc.; H. Wiggin, M.P.; Prof. W. C. Williams, B.Sc.; S. Young, D.Sc.

The Papers brought before the Section were as follows:—

President's Address.

Dr. W. J. Russell and W. Lapraik.—Absorption Spectra of Uranium Salts.

Prof. T. Carnelley.—The Air of Dwellings and Schools, and its Relation to Disease.

Alexander Pringle.—On some probable new Elements.

A. L. Stern.—Action of Bromine on Chlorides of Phosphorus.

Rev. A. Irving.—Dissociation and Contact Action.

Dr. Nicol.—Report of Committee on Vapour Pressures and Refractive Indices of Salt Solutions.

Prof. Ramsay.—Report of Committee on certain Physical Constants of Solution.

Discussion on the Nature of Solution, opened by Prof. Tilden.

Dr. Nicol.—Water of Crystallisation in Solution.

Dr. Perkin.—On the Magnetic Rotation of Mixtures of Water with some of the Acids of the Fatty Series, with Alcohol, and with Sulphuric Acid; and Observations on Water of Crystallisation.

Prof. Ramsay and Dr. Young.—On the Nature of Liquids.

Profs. Armstrong, Hartley, and Pickering, and Dr Gladstone continued the discussion.

Prof. W. N. Hartley.—On the Fading of Water-Colours.

R. Warrington.—Distribution of the Nitrifying Organism in the Soil.

Dr. Tidy.—Action of Drinking Water on Lead.

Prof. Odling.—Micro-Organisms in Drinking Water.

W. A. Shenstone.—Report of the Committee on the Influence of the Silent Discharge of Electricity on Oxygen.

H. B. Dixon, F.R.S.—Preservation of Gases over Mercury.

W. Crookes, F.R.S.—The Methods of Chemical Fractionation.

W. Crookes, F.R.S.—On the Fractionation of Yttria.

H. Robinson. The Colour of the Oxides of Cerium and its Atomic Weight.

Prof. Armstrong.—The Determination of the Constitution of Carbon Compounds from Thermo-Chemical Data.

E. F. Ehrhardt.—On the Relative Stability of the Mono-Hydrochlorides $C_{10}H_{17}Cl$, obtained from Turpentine and Camphene respectively.

Dr. R. F. Ruttan.—Derivatives of Tolidin and the Azotolidin Dyes.

J. W. Wailes.—Treatment of Phosphoric Crude Iron in Open Hearth Furnaces.

W. Hutchinson.—Notes on the Basic Bessemer Process in South Staffordshire.

G. Hatton.—Production of Soft Steel in a New Type of Fixed Converter.

T. Turner.—Influence of Re-melting on the Properties of Cast-Iron.

T. Turner.—Silicon in Cast-Iron.

T. Turner.—Influence of Silicon on the Properties of Iron and Steel.

T. Turner.—Estimation of Carbon in Iron and Steel.

Prof. Armstrong.—Report of Committee on Isomeric Naphthalene Compounds.

Dr. W. M. Watts.—Report of the Committee on Wave Lengths.

Dr. H. R. Mill.—Chemistry of Estuary Water.

Dr. Gladstone.—The Essential Oils: a Study in Optical Chemistry.

Dr. G. H. Bailey.—An apparatus for maintaining Constant Temperatures up to $500^{\circ}C$.

W. Thomson.—On a New Apparatus for Readily Determining the Calorimetric Value of Fuel or Organic Compounds.

Prof. Odling.—On some Decompositions of Benzoic Acid.

Dr. O. W. Huntington.—The Crystalline Structure of Iron Meteorites.

TO CORRESPONDENTS.

F. V.—Any operative chemist will supply you with apparatus for making oxygen, and any chemical text-book will tell you how to make it.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 17th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than Wednesday, the 15th prox.

NORMAL SCHOOL OF SCIENCE AND ROYAL SCHOOL OF MINES, SOUTH KENSINGTON AND JERMYN STREET.

DEAN—PROFESSOR T. H. HUXLEY, F.R.S.

Session 1886-87.

From the 1st October, 1886, till about the end of June, 1887, the Laboratories will be open to Students in the following Sciences:—

CHEMISTRY AND AGRICULTURE.

PHYSICS.

BIOLOGY.

GEOLOGY.

MECHANICS AND MECHANICAL DRAWING.

METALLURGY, MINING, AND ASSAYING.

The following Courses of Lectures will be given during the Session:—4th October, 1886, Mechanics, Professor T. M. Goodeve M.A.; Inorganic Chemistry, Professor Thorpe, F.R.S.; 5th October 1886, Elementary Zoology, G. B. Howes, Esq.; 7th October, 1886, Principles of Agriculture, J. Wrightson, Esq.; 11th October, 1886, Metallurgy, Professor W. C. Roberts-Austen, F.R.S.; 8th November, 1886, Mining, Professor Warrington Smyth, F.R.S.; 4th January, 1887, Elementary Botany, Dr. D. H. Scott; 15th February, 1887, Physics, Professor F. Guthrie, F.R.S.; Geology, Professor J. W. Judd, F.R.S.; Advanced Zoology, G. B. Howes, Esq.; Advanced Botany, Dr. D. H. Scott; Organic Chemistry, Dr. F. R. Japp, F.R.S.; Mineralogy, F. Rutley, Esq.; 15th June, 1887, Astronomical Physics, J. Norman Lockyer, Esq., F.R.S.

A course of Mine Surveying, conducted by Mr. B. H. Brough, will begin on the 15th February, 1887.

In addition to the above, lectures will be given in the Chemical Division by Drs. Hodgkinson and Percy Frankland; in the Physical Division by Messrs. Boys, Mitchell, Hoffert, and Captain W. de W. Abney, R.E., F.R.S.

For further particulars apply to the Registrar, Normal School of Science, South Kensington.

The LONDON HOSPITAL and MEDICAL COLLEGE, Mile End, E.

The SESSION 1886-87 will commence on Friday, October 1st, 1886: by that date the New College Buildings will be ready for occupation. The very extensive additions that have been made to the School Premises will afford complete provision for the teaching of all branches of Medical Science; the accommodation provided being more than double that which was provided in the Old Buildings. An inaugural ceremony will take place, of which due notice will be given.

FOUR ENTRANCE SCHOLARSHIPS, value £60, £40, £30, and £20, will be offered for competition at the end of September to new Students. Fees for Lectures and Hospital Practice, 90 guineas in one payment, or 100 guineas in three instalments. All Resident and other Hospital Appointments are free, and the holders of all the Resident Appointments are provided with rooms and board entirely free of expense. The Resident Appointments consist of five House Physiciancies, five House Surgeoncies, one Accoucheurship, and one Receiving-room Officer; four Dressers and four Maternity Pupils also reside in the Hospital. Special Classes for the Preliminary Scientific and Intermediate M.B. Examinations of the University of London and for the Primary and Pass Examinations for the Fellowship of the Royal College of Surgeons of England are held throughout the year. Special entries may be made for Medical and Surgical Practice. The London Hospital is now in direct communication by rail and tram with all parts of the metropolis, and the Metropolitan, Metropolitan District, East London, and South-Eastern Railways have stations within a minute's walk of the Hospital and College.

For prospectus and particulars apply, personally or by letter, to
MUNRO SCOTT, Warden.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

In the matter of Letters Patent granted to ALEXANDER DEMPSTER, of Elland, Yorkshire, for "Improvements in apparatus for distilling ammoniacal liquor for the purpose of producing sulphate of ammonia," dated 8th March, 1886, No. 3220.

NOTICE IS HEREBY GIVEN that the said Alexander Dempster has applied for leave to amend the specification numbered as above.

A copy of the Specification as proposed to be amended can be inspected at the Patent Office, and full particulars of the proposed amendment were set forth in the Official Journal of the Patent Office issued on the 3rd September, 1886.

Any person intending to oppose the said application must leave particulars (on Form G) of his objections thereto at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date hereof.

Dated this 3rd day of September, 1886.

(Signed)

J. CLARK HALL,
Deputy Comptroller-General.

Silicates of Soda and Potash in the state of Soluble Glass, or in CONCENTRATED SOLUTION of first quality, suited for the Manufacture of Soap and other purposes, supplied on best terms by W. GOSSAGE and Sons, Soap Works, Widnes, Lancashire.
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THE CHEMICAL NEWS.

VOL. LIV. No. 1399.

ADDRESS TO STUDENTS.

ONCE more our scientific institutions are resuming their activity, and students are considering the important questions what, where, and above all, how they shall study. Those who intend devoting themselves exclusively or mainly to chemical science will find themselves in various respects placed in a more advantageous position than were their predecessors. The number of colleges and schools where chemistry is taught has increased and is still increasing. Even upon the conductors of the old grammar schools the truth is at last slowly dawning that the arts of observation and of drawing right conclusions from our observations are very important points in education, and that these arts can scarcely be acquired without a training in at least one branch of the physical or natural sciences.

But not merely is the study of chemistry more widely introduced in schools and colleges than heretofore. It is taught by abler men and in laboratories much better fitted with the needful appliances. Here we must guard against a common error. We are often told of the simplicity of the apparatus with which Davy, Dalton, and Graham made important experiments and arrived at valuable results. But this is precisely analogous to what we observe in gold seeking. When a gold field has been recently discovered the digger may secure a rich store of treasure with very simple appliances. But by and by the nuggets are all extracted, and to obtain further supplies of the precious metal it is necessary to mine for auriferous reef, to grind it, and to extract the gold by amalgamation. For these purposes powerful and costly plant is needed.

Now, a precisely similar change is come over chemistry. The phenomena which, so to speak, lay near the surface have been already observed and put on record. If we wish to go on in the career of discovery we must dig deeper. We must make use of instruments of precision which previous investigators did not require. Hence it is a just subject of congratulation if our laboratories are more adequately equipped than were those of Davy and Dalton.

But whilst we rightfully rejoice over the multiplied and improved facilities for study and research, we must ask ourselves whether the play is becoming more and more worthy of the candle; whether the researches conducted in the present day show a sufficient improvement in quantity and quality, as compared with those carried on in this country in the first half of the present century, or with those engaged in abroad? Are we gaining ground, and, if not, why not? We must remember that in higher education, as in other spheres, "one fundamental error can vitiate centuries of national life." A great country has furnished us with a warning example. That country, more perhaps than any other, has placed the highest value upon mental culture, as the only passport to rank and office; it has covered its vast territory with elementary schools, intermediate schools, and universities, and it has invented and practised for ages competitive examination. And

what has been the result? A complete arrest of mental development. As Professor Benedict aptly puts it, in China "learning is ceaseless repetition, its education has become a pitiable mummery, finding its supreme test in an act of memory."

Now it surely behoves us to inquire in how far the picture thus drawn of China is applicable to us. What are we cultivating, the art of origination, or merely that of repetition? Are we learning to *do* things or merely to talk about them? Knowledge is certainly power, but there is knowledge and knowledge. A student, for example, might conceivably know by heart the whole of "Watts's Dictionary of Chemistry," and might have a verbal understanding of the whole. Yet he might be unable to perform the simplest analysis, or to apply his knowledge to any practical purpose, much less conduct any experimental research. Now we are not at all anxious for an increase in the number of such men. We consider that a man who is able to add to our knowledge by making even the simplest observation is far more truly entitled to the name of chemist, even though his memory were but scantily stocked with chemical facts.

Faraday is known to have declared that he could never understand the meaning of an experiment until he had performed it himself. How, then, are men of merely average intelligence to understand experiments by merely reading about them? The main objects of the true student, in any department of physical and natural science, are how to observe, how to systematically interrogate Nature, and how to draw right conclusions from the phenomena observed. In proportion as he succeeds in so doing he is likely to be efficient either in abstract science or in the arts. In proportion as a system of education fails in instilling these lessons it becomes a road leading to that stagnation of national intelligence into which China has fallen.

Well does Mr. Patrick Geddes say:—"For two distinct tendencies are at work in our modern universities and schools, the dominant one deliberately preferring memory of mere words to observation of facts and reasoning therefrom, which should be supplied by *discipline* in science, and more memory of words to that coordination of hand and eye which is supplied by practice in the arts and substituting verbal test of competitive examination for practical test in life." *Discipline* in science, not memory of science, is the object to be pursued.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree granted by this University are required to have passed the Matriculation Examination, to which no candidate is admitted unless he has produced a certificate showing that he has completed his sixteenth year.

The Fee for this examination is £2.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the third Monday in June. The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the Candidates to pass, *viva voce* questions to any Candidate in the subjects in which they are appointed to examine.

Candidates are not approved by the Examiners unless

they have shown a competent knowledge in each of the following subjects:—Latin. Any two of the following Languages:—Greek, French, German, and either Sanskrit or Arabic. The English Language, English History, and Modern Geography. Mathematics. Natural Philosophy. Chemistry.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds—their chief physical and chemical characters—their preparation—and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each Candidate who applies for it, after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any Candidates in the Honours Division of not more than Twenty years of age at the commencement of the Examination possess sufficient merit, the first among such Candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such Candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments, provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any Candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held in July, 1887.

No Candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Candidates will be examined as follows:—For a Pass or for Honours in (1) Inorganic Chemistry, (2) Experimental Physics, (3) Mathematics; and for a Pass only in (4) General Biology. Candidates may also be examined for Honours in Botany and in Zoology.

Every Candidate, on sending in his name for the Examination, must state whether he intends to compete for Honours in any subject or subjects; and if he does so intend, must specify the subject or subjects.

No Candidate will be allowed to take both the Pass and the Honours Papers in the same subject, but every Candidate must take the Pass Papers in those subjects in which he does not offer himself for Honours.

A Candidate who enters for, but fails to obtain, Honours in Inorganic Chemistry, Experimental Physics, and Mathematics, may be recommended by the Examiners for a Pass in these subjects respectively, if they are satisfied that he has shown such a competent knowledge thereof as is required by the Regulations for the Pass Examination.

The Examiners will make no report upon the Examination for Honours of a Candidate who has failed in any part of his Pass Examination.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the

Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.SC. EXAMINATION.

The B.Sc. Examination will be held in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

The regulations are framed with the view of allowing the candidate to select *any three* of the following nine subjects:—

1. Pure Mathematics.
2. Mixed Mathematics.
3. Experimental Physics.
4. Chemistry.
5. Botany, including Vegetable Physiology.
6. Zoology.
7. Animal Physiology.
8. Physical Geography and Geology.
9. Mental and Moral Science.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical exercises in Simple Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

The Fee for this Examination is £10.

Every Candidate for the degree of D.Sc. must forward a statement in writing of the special subject within the purview of the Faculty of Science, as set out in the programme of the B.Sc. Examination, upon a knowledge which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. The Dissertation or Thesis shall have been written in view of candidature, or shall have been published within the two academical years immediately preceding. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published, and every contribution so specified and submitted shall be considered and taken as part of his qualification for the degree. Candidates for the degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No Candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination, nor unless he have given notice of his intention to the Registrar at least one calendar month before the commencement of the examination.

The Fee for this examination is Five Pounds.

Candidates for the Pass Examination, whether in January or July, will be allowed either to take all the three subjects of the Examination—(a) Inorganic Chemistry, (b) Experimental Physics, and (c) General Biology—at the same Examination, or to take them at two separate Examinations,—that is to say, two subjects at the first Examination for which they may enter, and one subject at the second Examination; or, reversely, one subject at the first Examination, and two at the second.

Candidates at the July Examination who enter for the whole Examination will be examined as follows:—For a Pass or for Honours in (a) Inorganic Chemistry, (b) Experimental Physics; and for a Pass in (c) General Biology. Candidates who have entered for the whole Examination may also be examined for Honours in Botany and in Zoology.

Every Candidate, on sending in his name for the July Examination, must state whether he intends to compete for Honours in any subject or subjects; and, if he does so intend, must specify the subject or subjects.

No Candidate will be allowed to take both the Pass and the Honours Papers in the same subject; but every Candidate must take the Pass Papers in those subjects in which he does not offer himself for Honours.

A Candidate who enters for, but fails to obtain, Honours in Organic Chemistry or Experimental Physics may be recommended by the examiners for a Pass in these subjects respectively, if they are satisfied that he has shown such a competent knowledge thereof as is required by the Regulations for the Pass Examination.

EXAMINATION IN SUBJECTS RELATING TO PUBLIC HEALTH.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Professor of Mineralogy.—N. S. Maskelyne, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

More detailed information may be obtained from the University Calendar; from the professors; from E. Chapman, Esq., M.A., Frewin Hall; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or second term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £80 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

The following are the Lectures on Chemistry for the ensuing Academical Year:—

MICHAELMAS TERM, 1886.

General Course, by the Professor of Chemistry, on Tuesdays, Thursdays, and Saturdays, at 12 noon. Begin Oct. 12.

Dissociation and Thermal Chemistry (Advanced), by the Jacksonian Professor, on Mondays, Wednesdays, and Fridays, at 12 noon. Begin Oct. 13.

Thermo Chemistry, by Mr. Main, at St. John's College, on Tuesdays, Thursdays, and Saturdays, at 10 a.m. Begin Oct. 12.

General Principles (elementary) by Mr. Pattison Muir, Caius College, Monday, Wednesday, and Friday, at 10 a.m. Begin Oct. 13.

General Principles (Advanced), by Mr. Pattison Muir, Caius College, Tuesdays, Thursdays, and Saturdays, at 10 a.m. Begin Oct. 14.

Elementary Organic Chemistry, by the Assistant to the Jacksonian Professor, on Mondays, Wednesdays, and Fridays, at 1 p.m. Begin Oct. 13.

General Principles (Non-metals) for Natural Science Tripos, by Mr. Heycock, at King's College, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin Oct. 13.

Organic Chemistry, by Mr. R. M. Lewis, at Downing College, on Tuesdays, Thursdays, and Saturdays, at 9 a.m. Begin Oct. 12.

Practical Chemistry, by the Demonstrators of Chemistry. University Laboratory. Also at St. John's, Caius, and Sidney Colleges. Daily. Begin Oct. 12.

LENT TERM, 1887.

General Course continued, by the Professor of Chemistry, on Tuesdays, Thursdays, and Saturdays, at 12 noon. Begin Jan. 15.

Spectroscopic Chemistry, by the Professor of Chemistry, on Tuesdays, at 1.30. Begin Jan. 15.

Organic Chemistry, by the Jacksonian Professor, on Mondays, Wednesdays, and Fridays, at 12 noon. Begin Jan. 17.

General Course of Chemistry, by Mr. Main, at St. John's College, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin Jan. 17.

General Principles (continued) by Mr. Pattison Muir, at Caius College, on Tuesdays, Thursdays, and Saturdays, at 10 a.m. Begin Jan. 18.

Principles of Chemistry, Elementary (continued), by Mr. Pattison Muir, Caius College, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin Jan. 27.

Methods of Organic Analysis, by the Assistant to the Jacksonian Professor, on Mondays, Wednesdays, and Fridays, at 1 p.m. Begin Jan. 17.

Chemical Philosophy, by Mr. Heycock, King's College, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin Jan. 17.

Practical Chemistry, at the University Laboratory, and at St. John's, Caius, and Sidney Colleges, daily. Begin Jan. 17.

EASTER TERM, 1887.

Elementary Chemistry, by a Demonstrator, on Mondays Wednesdays, and Fridays, at 12 noon. Begin April 22.

General Course continued, by Mr. Main, at St. John's College, on Mondays, Wednesdays, and Fridays, at 10. Begin April 22.

Elementary Course for first M.B. (continued), including Carbon Compounds, by Mr. Pattison Muir, at Caius Laboratory, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin April 22.

Gas Analysis, by the Assistant to the Jacksonian Professor, on Mondays, Wednesdays, and Fridays, at 10 a.m. Begin April 22.

Aromatic Bodies, on Tuesdays, Thursdays, and Saturdays.

Practical Chemistry, at the University Laboratory, at St. John's College, at Caius College, and at Sidney College, daily. Begin April 22.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE.)

Professor of Chemistry.—C. L. Bloxam, F.C.S.

Demonstrator of Practical Chemistry.—J. M. Thomson, F.C.S.

Assistant Demonstrator.—G. S. Johnson, F.C.S.

Chemical Tutor.—Herbert Jackson, F.C.S.

On Tuesday and Friday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures, of Metallurgy, and of Domestic Economy, are explained and illustrated.

Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till

four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—One Month (daily attendance), £4 4s. od.; Three Months (daily attendance), £10 10s. od.; Six Months (daily attendance), £18 18s. od.; Nine Months (daily attendance), £26 5s. od. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1886-87, are Tuesday, September 28, Tuesday, January 11, and Wednesday, April 20.

NATURAL PHILOSOPHY.

Professor.—W. G. Adams, M.A., F.R.S.

Demonstrator.—H. Tomlinson, B.A.

Assistant Demonstrator and Tutor.—E. F. Herroun.

The following Classes are held for Students preparing for the Science Examinations of the University of London, Indian Civil Service, and other public examinations, and for those who are studying Natural Philosophy as a part of a liberal education, or who intend to devote themselves to Civil, Mechanical, or Electrical Engineering.

Mechanics.—(1) A Course of between Fifty and Sixty Lectures on Elementary Mechanics and Hydrostatics. (2) A more advanced Course of between Eighty and Ninety Lectures on Theoretical and Applied Mechanics.

Experimental Physics.—(3) A Course of between Fifty and Sixty Lectures on Experimental Mechanics, Hydrostatics, Pneumatics, and Heat. (4) A Course of about Thirty Lectures on Heat, Light, and Sound, or Electricity and Magnetism in alternate years. (5) A Course of Demonstrations and Practical Work on Heat, Light, Electricity, and Magnetism.

Fees for either Course separately, including one Course of Mechanics, £4 4s. per Term or £10 10s. per annum.

(6) A Course of Practical Laboratory Work for Students preparing for the Preliminary Scientific and Intermediate Scientific Examinations.

Monday and Thursday, 2 to 4 p.m.

Fees:—£3 3s. per Term or £8 8s. per annum.

(7). A Tutorial Class in Experimental Physics for the Preliminary and Intermediate Scientific Examinations.

Tuesday and Friday, 10.15 to 12.15 a.m.

Fees:—£2 2s. per Course.

EVENING CLASSES.

(a) A Winter Course of Lectures on Mechanics, Hydrostatics, and Pneumatics on Monday and Thursday Evenings from 6 to 7 p.m. October to March.

(b) A Summer Course on same subjects on Thursday evening, 6.30 to 8 p.m. April to June.

(c) A Winter Course of Lectures on Experimental Physics on Wednesday Evening, 7 to 8 p.m.

(d) A Course of Practical Work in the Laboratory. Thursday Evening from 7 to 9 p.m. October to March.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

Demonstrator.—W. G. McMillan.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of

Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

Fees:—Lectures only, £3 3s. The laboratory fees are arranged for continuous work and intermittent work, and special arrangements as to attendance may be made with the Professor.

Two courses of lectures will be delivered on Monday evenings by Mr. W. G. McMillan, in which especial attention will be devoted to the requirements for the examination of the City and Guilds of London Institute, viz., a Course on the "Properties of Metals and Alloys and their Uses in the Arts," and a Course on "Fuels, their Uses and Economy." A Practical Metallurgical Class will be held on Friday evenings, at which students may prepare for the examination of the Science and Art Department in Practical Metallurgy.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June. The next Winter Course will begin on Monday, October 4th, and will terminate on Friday, April 1st, 1887, the last fortnight being devoted to examinations. Many of these classes have special reference to the B.A. and Matriculation Examinations of the University of London.

Agriculture.—A Course of Lectures on this subject will be given during the ensuing Winter by Mr. Frederick James Lloyd, F.C.S., Consulting Chemist to the British Dairy Farmers' Association. The Lectures will be given on Friday Evenings at 6 p.m., beginning October 8th, 1886.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—Alex. W. Williamson, Ph.D., LL.D., F.R.S.

Lecturers.—Henry Forster Morley, M.A., D.Sc.; R. T. Plimpton, Ph.D.

Assistants.—E. E. Graves, F.C.S.; S. Rideal, D.Sc., F.C.S.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Wednesday, October 6th, until Saturday, December 18th;

Second Term, from Tuesday, January 11th, 1887, till Tuesday, March 29th;

Third Term, for Lectures, from Tuesday, April 19th, till Saturday, June 18th. Class Examinations occupy about ten days, beginning on Monday, June 20th.

Students, who having entered in October do not intend to present themselves in all three subjects at the July Preliminary Science Examination, should during the first term confine their attention to Chemistry, and take this subject alone at the January Examination.

Students entering in January should take Physics and Biology at the July Examination, and Chemistry at the succeeding January Examination.

The Special Course on the Metals will be given by Mr. Rideal on Monday, Wednesday, and Friday, at 10.

Introductory or Matriculation Course.

Tuesday, Wednesday, Thursday, and Friday, at 11, commencing May 4, 1887. Fee:—£4 4s.

The Course will consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

General Course of Chemistry and Chemical Physics.

First and Second Terms: Inorganic.—The Class meets five times a week: Mondays, Wednesdays, and Fridays, at 11, for Lectures or Examinations; and on Tuesdays and Thursdays, at 9, for Exercises.

Third Term: Elementary Organic.—Lectures or Exercises, Tuesdays, Wednesdays, and Fridays, at 11.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £3 3s.; for the Third Term, £2 2s.

The subjects treated in the First Term of the Course include those required in Chemistry at the Matriculation Examination of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Extra Meetings of the Exercise Class in connection with the General Course will be held in the Third Term for those Students who intend to present themselves for the Preliminary Scientific or Intermediate Science Examination in July.

The Third Term provides instruction in the preparation, composition, and fundamental properties of the most common important organic substances. The subjects dealt with include those required by Candidates for the First Examination under the conjoint scheme. The last three Meetings will be devoted to recapitulation.

Advanced Course of Inorganic Chemistry.

Third Term:—Monday, Wednesday, and Friday at 4.

Fee:—£2 2s.

The Course will consist of about Thirty Lectures, and is intended as a supplement to the General Course. It includes the subjects required for the Honours Papers in the Preliminary Scientific and Intermediate B.Sc. Examinations and the Additional Inorganic Chemistry for the B.Sc.

Organic Chemistry.

Tuesday and Thursday at 11, Saturday at 9, in the First Term; Monday, Wednesday, and Friday, at 9, in the Second Term; and Tuesday and Thursday, at 9, in the Third Term, beginning Wednesday, October 6th. The hour of meeting will be altered should the Class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the First and Second Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

Practical Class.

First and Second Terms, on Tuesday and Thursday, at 11 or 10. Each Student will attend twice a week, at the hour allotted to him, on arrangement with the Professor.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific, Intermediate B.Sc., and Conjoint Scheme Examinations.

Senior Practical Class.

Mondays and Saturdays from 10 to 12 during the Third Term.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Matriculation Course. (Women.)

Lectures: Wednesday and Friday, from 4 to 5.

A Class of Elementary Chemistry, including the subjects required for Matriculation, will be given during the Second and Third Terms, commencing Wednesday, January 12th.

Fee:—For the Course, including the cost of apparatus and materials, £4 4s.; for the Third Term, £2 12s. 6d.

Inorganic Chemistry. (Women).

Lectures and Practical Work: Wednesday at 3, Thursday at 12, Friday at 11, Saturday at 10, during the First and Second Terms, beginning on Wednesday, October 6th. The time of meeting will be altered to suit the convenience of the Class.

This Class includes the subjects required for the Preliminary Scientific and Intermediate B.Sc. Examinations. An elementary knowledge of Chemistry will be expected from students joining the class. Simple Qualitative Analysis will be practised by the Students.

Fee, including cost of apparatus and materials, £7 7s.; for the Second Term, £4 4s.

Quantitative Analysis.

A Course of Ten Lectures on the newer methods of Quantitative Analysis will be given during the Second Term, on Mondays, at 4. Fee, £1 1s. Some of the more important operations and methods of Quantitative Analysis will be described, including some of the best methods which are of too recent introduction to have found a place in the ordinary text-books.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays, 9 a.m. to 2 p.m., from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate B.Sc., B.Sc., D.Sc.

Students who wish to attend the Laboratory and Classes of Technical Chemistry may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Chemistry and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by Students entered for the Session.

Chemical Technology.

Professor CHARLES GRAHAM, D.Sc., F.I.C.

Assistants.—C. J. Wilson, F.C.S., and W. J. Scrutton.

The Course of instruction in this Department is designed to afford to Students who propose to devote themselves to industrial pursuits in which Chemistry plays an important part, or to prepare themselves for the profession of Consulting Chemist, the instruction essential for their success in their future line of work. It will also be found of great value in two of the branches (Organic and Inorganic Chemistry) in which the Degree of Doctor of Science can be taken at the University of London.

In the Session 1886-87, it is proposed to treat of the following subjects:—

Heating and Lighting.

Metallurgy.

The Chemistry of the Alkali trade.

Agricultural Chemistry.

Fees—for each Course, £2 2s.; for two Courses, £3 3s. for the four Courses, £5 5s.

Courses of Lectures will also be delivered on the Chemistry of Brewing (fee, £3 3s.), and on Chemistry in its relation to Engineering and Architecture (fee £2 2s.).

Laboratory of Chemical Technology.

The instruction in the Laboratory of Chemical Technology will consist of the examination and valuation of raw materials used, and of the final products obtained in various manufacturing industries, and of experimental examination of the processes employed in the arts and manufactures.

The Laboratories are open daily from 9 a.m. to 4 p.m., from the 6th of October until the middle of July, with a short recess at Christmas and at Easter.

Fees—for the Session, 25 guineas; six months, 18 guineas; three months, 10 guineas; one month, 4 guineas; exclusive of the expense of materials.

Residence for Students.

Students can obtain residence at University Hall, Gordon Square. Particulars can be obtained of the Dean, Dr. H. Forster Morley, on application.

NORMAL SCHOOL OF SCIENCE AND
ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

Assistant Professor.—F. R. Japp, M.A., Ph.D., F.R.S.

Demonstrators.—W. R. Hodgkinson, Ph.D., and P. F. Frankland, Ph.D., B.Sc.

Assistants.—G. S. Newth and H. Chapman Jones.

The Normal School of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is affiliated to the Normal School. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Normal School. The instruction in the Normal School is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Normal School, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Normal School of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction is the same for all the divisions during the first two years, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins about the 1st of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third and fourth years, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Admission is granted to persons desirous of attending certain courses of the lectures without the laboratory instruction, on payment of the lecture fees.

The fees which are shown in the following table must be paid to the Registrar of the School before the commencement of each course.

		Part I.	Part II.	Part III.	Part IV.
		Lecs.	Lab.	Lecs. & Lab.	Lecs. & Lab.
		£	£	£	£
Chemistry	3	13	16	16	
Physics	5	12	12	12	
Biology with Botany	5	12	12		
Geology with Mineralogy	4	8	8	8	
Mechanics	4	6	8	8	
Metallurgy	2	13	15		
Mining	4	6			
Agriculture	4	10			
Astronomy	2				

Mathematics and Mechanical Drawing £3 per term. Geometrical Drawing, £3 per session. Freehand Drawing, £1 per term.

Thus the fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Normal School of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Science teachers actually engaged in teaching who are registered by the Science and Art Department as qualified to earn payments for teaching Science may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 2nd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £2 each. (See Science Directory.)

Working Men's Lectures.—Three courses of evening lectures for working men will be given during the session in Chemistry, Zoology, and Mechanics. The admission to each course of six lectures will be 6d. The number of tickets is limited by the size of the lecture theatre.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor of Chemistry and Experimental Physics.—T. S. Humpidge, Ph.D., B.Sc. (Lond.)

The College is open to male and female students not under the age of 15 years. The Session begins on Tuesday, September 21st.

The Courses will be as follows.—I. Introductory and Chemistry of the Non-Metals, during Michaelmas Term. II. Chemistry of the Metals and Chemical Theory, during Lent Term. III. Organic Chemistry and Advanced Theoretical Chemistry, during Easter Term.

Course I. will suffice for the requirements of the London University Matriculation and other similar examinations. Candidates for the Intermediate B.Sc. and Preliminary Scientific (M.B.) Examinations will require Course II. as well, and must also take a course of practical instruction in the Chemical Laboratory. Course III. will meet the

requirements of Students taking Chemistry in the B.Sc. and other advanced examinations.

In connection with Courses I. and II. there will be Exercise Classes meeting once a week.

The Lectures will be delivered and the Exercise Classes will meet on Tuesdays, Wednesdays, Thursdays, and Fridays at 10 a.m.

Practical Chemistry.—The Laboratory is open to Students daily during the Session from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except Saturdays.

Special courses will be arranged for those Students who intend following Medicine, Pharmacy, Agriculture, Applied Chemistry, or other professions in which a knowledge of technical chemistry is required.

The Fee for the whole Session, paid in advance, is £10; if paid by single Terms, for the first Term of attendance in each Session £4; for the second Term, £3 10s.; for the third Term £3. The Fee for Practical Chemistry, or Practical Physics, is 5s. per Term extra. Any person wishing to attend single classes may do so on payment of the sum of £1 per Term for each class.

Several valuable Scholarships and Exhibitions are attached to the Studentship.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—J. W. James, Ph.D., F.C.S.

The Session commences in October and terminates in June, and is divided into three terms.

The Junior Course (delivered during the summer term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s.

The Intermediate Course consists of 90 lectures in continuation of the Junior Series, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Tuesdays, Thursdays, and Saturdays at 12. Fee £3 3s.

The Senior Course will occupy about two terms, and includes some 90 lectures devoted to Organic Chemistry; Tuesdays, Thursdays, and Saturdays, at 9. Fee, £3 3s.

A course of 30 lectures on Qualitative and Quantitative Analysis and Chemical Calculations, on Wednesdays at 10.

The Laboratory Course may be modified to meet the requirements of individual students wishing to obtain a special knowledge in some branch of manufacturing or industrial chemistry. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours, £4 4s. per term.

Evening Lectures.—A course of Lectures will be given on Elementary Chemistry. Courses of lectures on Chemistry and the Iron and Steel Manufacture will also be delivered in certain towns in South Wales in connection with the local lecture scheme.

At the entrance examination in September, and the annual examination in June, several scholarships, &c., are awarded.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—W. Ramsay, Ph.D.

Lecturer.—Sydney Young, B.Sc.

The session 1886—87 will begin on October 5. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. Excursions to some of the mines, manufactories, and chemical works of the neighbourhood are occasionally made. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering

and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College.

DAY LECTURES.

Inorganic Chemistry.

Junior, Senior, and Advanced Classes.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 9 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Tuesdays, Thursdays, and Saturdays at 10 o'clock.

Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will close at 1 p.m. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer.

Fees in Guineas—

	6 Days a Week.	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.
Per Session	17	15	13	10	7½
„ Two Terms ..	13	11	9	7½	5½
„ One Term ..	7	6	5	4	3
„ Month	3	3	2	2	1½

Students may arrange to divide their days of laboratory work into half-days.

Photographic Chemistry.

A Course of Lectures will be given by Mr. A. Richardson, Ph.D., on Mondays at 10, which will cover the subject as prescribed for the Technological Examination of the City and Guilds of London Institute; fee, £1 1s. for each term. The Photographic Laboratory is open from 10 to 5 every Wednesday; fee, £3 3s. for each term. A Course of Evening Lectures on the same subject will also be given on Fridays at 7.

EVENING LECTURES.

Lecturer.—Sydney Young, B.Sc.

Wednesday and Friday, 8 to 9.

This course will consist of Two Lectures a week during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures.

Fee, 15s. for Two Terms; 10s. for One Term.

A Course of Lectures will also be delivered on Monday evenings at 8, on the Chemistry of Every-day Life.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

With the approval of the Council of the Institute of Chemistry students desiring to qualify as Associates may pass through the requisite amount of study at this College, which has also been approved as a centre for the Practical Examination of the Institute.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc., Lond., F.R.S.

Assistant Lecturer.—W. W. J. Nicol, M.A., D.Sc., Edin.

Demonstrator.—Thomas Turner, F.C.S.

The Session will be opened on Friday, October 1st, 1886.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays, at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on *Inorganic Chemistry* (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Spring and Summer Term) which relates to *Organic Chemistry*.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About one hundred lectures on *Inorganic Chemistry and Chemical Philosophy* will be given on Mondays, Tuesdays, Wednesdays, Thursdays, and Fridays, at 9.30 a.m. Fee, £3 3s. for a single term, or £5 5s. for the course from October to March.

2. January to June (Spring and Summer Terms). About fifty lectures will be given on *Organic Chemistry*, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday, at 9.30 a.m. Fee, £2 2s.

In all these courses the instruction will often take the form of class teaching, and exercises will be set which students will be expected to work at home.

Laboratory Practice.

The College Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health may be taken in the Mason College Laboratory.

The Ordinary Course for Medical Students is given on Tuesdays and Thursdays from 2 to 4 p.m. throughout the Summer Term.

Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Three Terms	18 „	12 „

A Course of short demonstrations and exercises will be given by the Professor or one of his Assistants once a week. All first-year Students will be required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.—A Course of Twenty Lectures will be given in the Winter Term (October to Christmas), on Tuesday and Friday Afternoons at 2.30, on the Principles and Practice of Metallurgy. Fee, £1 1s. After Christmas a Course of Lectures will be given on Iron and Steel.

Arrangements have been made in the Chemical Laboratory for giving instruction in Practical Metallurgy.

Evening Classes.

A Course of Twenty Lectures on Elementary Chemistry will be given by Dr. Nicol during the Winter and Spring Terms, on Fridays at 8. Fee, 10s.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing.—Edmund Knecht, Ph.D.

Assistant.—Charles H. Jessop.

The school year is divided into three terms, and the Session commenced on September 7th and terminates at the end of July.

The course of instruction extends over two years, and embraces Day and Evening Classes and Practical Laboratory work in Chemistry, Dyeing, and Metallurgy.

The tuition fees are arranged for two classes of students, those paying a reduced sum being expected to sit for the Government Science examinations.

Several exhibitions and scholarships are available for students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of of manures, soils, waters, feeding stuffs, dairy products, and

other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.C.S.

Assistant Lecturers.—C. H. Bothamley, F.C.S., and Herbert Ingle.

The Session begins October 4, 1886.

Lecture Courses.

1. General Course on Systematic Chemistry—Monday, Tuesday, Thursday, and Friday, at 4 p.m., from October to the end of the second term. Fee for the Course, £5 5s.

2. Lectures on Laboratory Practice and Chemical Calculations—Monday, at 12.30 during the First and Second Terms. Fee, £1 1s.

3. Chemistry as Applied to Coal Mining—Wednesday, during the First Term, at 5.30 p.m.

4. Organic Chemistry—Tuesday and Thursday at 12.30 p.m., during the Second and Third Terms. Fee £2 12s. 6d.

5. Lectures on Chemical Technology—Will be varied from session to session. During Session 1886-7 a Course of Lectures "On Fuel" will be given on Wednesdays, at 4 p.m., during the Second and Third Terms. Fee £2 2s.

6. A Class on Elementary Chemistry, consisting of about Twenty-five Lessons, on the Non-metals, will be held on Saturdays, at 12.30 p.m. Fee for the Lecture Class, 10s. 6d.

7. Photographic Manipulation—A Course of Ten Lessons will be given on Fridays, from 2 to 5, during the Third Term, with special reference to dry plate processes and silver and platinum printing. Fee, £1.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Evening Classes.

A Course of twenty Lectures by Mr. C. H. Bothamley, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 13. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.C.S.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators.—C. A. Kohn, B.Sc., Ph.D., S. G. Rawson, B.Sc.

Assistant.—G. E. Harrison.

The new Chemical Laboratories being now open, the system of teaching in this department has been reorganised so as to afford greater facilities for acquiring a practical

acquaintance with Chemistry in its higher branches, and at the same time give Junior Students a thorough training in the elements and principles of the science. All Students are in the first stages taught alike, and as they advance they may select the branch or methods which they prefer, or which are most suited to their requirements. Besides the Chemical Lecture Theatre, seating 230, a smaller class room and a Practical Theatre accommodating 52 Students in Elementary Practical Chemistry and Qualitative Analysis, ample accommodation is provided for about 40 more advanced Students. An elaborately fitted room is provided for Organic work, which will be used temporarily as a Quantitative Laboratory, while organic operations will be carried on in a second organic room containing arrangements for combustions, operations in sealed tubes, and other special operations. Separate rooms are provided for Water Analysis, Gas Analysis, Photometry and Photography, Spectroscopic and Microscopic work. There is a balance Room, a Furnace Room, besides Stores, Service Rooms, Lavatories, and a separate room for ladies. The teaching is aided, especially in the Organic branch of the science, by a Chemical Museum. A dynamo will shortly be provided and will be used for experiments in the reduction of metals and other work employing electricity. The courses are intended to instruct the Student in Chemical Manipulation, Qualitative and Quantitative Analysis, Gas, Water, and other special branches of analysis, Organic Synthesis, Spectroscopy, and in the method of performing Chemical Researches, and making investigations with the view of applying Chemistry to Manufactures, Agriculture, or Hygiene, or to aid in the study of other sciences.

The Session commences October 4th.

Students desirous of having a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemistry as a profession, must devote at least three years to special study. They ought to have an ordinary school acquaintance with English Composition and Latin, and must be proficient in Arithmetic and the elements of Algebra.

They are recommended to adopt the following curriculum:—

First Year.—Chemistry—Course of Lectures on Theoretical Chemistry during the Autumn and Lent Terms; Chemical Laboratory, two days a week, during the Lent and Summer Terms; and the Practical Chemistry Class. Mathematics, Pure and Applied, Physics or Geology, Engineering Drawing and Design, French or German.

Second Year.—Chemistry—Second Attendance on portions of the Lecture Courses, if necessary; Lectures on Organic Chemistry; Chemical Laboratory, three days per week, and the Practical Organic Class during the Summer Term; Technological Chemistry. Physics, Mathematics, German or French.

Third Year.—Any of the above-mentioned lectures which have not been attended. Lectures on Organic Chemistry; Lectures on Chemical Philosophy; Chemical Laboratory, four or five days per week; Technological Chemistry; Physical Laboratory, one day per week.

Special Certificates will be granted to those Students who pass through the above or a similar curriculum, and who perform their work and pass the periodical examinations to the satisfaction of the Professors; but these Certificates of Proficiency will only be given to such as can perform Practical Work in a reliable manner. Remunerated appointments are occasionally offered to efficient Students of the third year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be awarded in December on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Laboratory is opened for Students from 10 a.m. to 5 p.m. daily, on Saturdays from 10 to 1 only.

The Prospectus containing full particulars may be

obtained from Adam Holden, 48, Church St., Liverpool, price 6d.; or from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.G.S., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty-five guineas, or per session of three months ten guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

UNIVERSITY OF DURHAM. COLLEGE OF PHYSICAL SCIENCE, NEWCASTLE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Demonstrator.—Saville Shaw.

The Session will commence on September 27th, 1886.

Junior Division: First Year Course.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be servicable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 9.30 a.m., and will commence on Wednesday, October 6th.

Senior Division: Second Year Course.—A Course of about sixty Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Tuesday, October 5th.

Fee, for either Course, five guineas for the Session.

A Special Course will be given on Applied Chemistry, commencing Thursday, October 7th. Fee, £2 2s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to

satisfy the examiners in three, at least, of the four subjects,—Mathematics, Physics, Chemistry, and Geology,—in an examination, to be held at the beginning of his second year.

The examination in Chemistry comprises:—General Principles of Chemistry. Elements of Inorganic Chemistry. Elements of Qualitative Analysis, including a Practical Examination.

The examination in Chemistry for Candidates at the end of their second year comprises:—Elements of Organic Chemistry and Applied Chemistry. Advanced Qualitative Analysis, including a Practical Examination. Elements of Quantitative Analysis.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

Candidates must send their names to the Secretary, on or before the 18th of September, and specify, at the same time, the special subject in which they desire to be examined.

The examination will be held at the College, and will commence on Monday, September 27th.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,

VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical and Metallurgical Laboratories.—(Vacant).

Professor of Organic Chemistry.—C. Schorlemmer, F.R.S.

Lecturer on Technological Chemistry.—Watson Smith, F.C.S., F.I.C.

Demonstrators and Assistant Lecturers.—Watson Smith, F.C.S., Harry Baker, F.C.S., Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc.

The Session begins on October 5, 1886, and ends on June 24, 1887.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Technological Chemistry.

Persons desiring to attend this course will be required to enter the College under the ordinary conditions of studentship.

The object of this course is to offer to students intending to devote themselves more especially to Applied Chemistry as complete a training as the College can provide in those branches of instruction which form the scientific foundation of the subject.

The complete course of instruction extends over four years, and embraces the following subjects:—

First Year.—Chemistry Lectures, Junior. Preparatory:—Chemical Laboratory, two days per week, and Analytical Chemistry Lectures class. Mathematical class, Section I. Experimental Mechanics. Geology (Physiography). French or German. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Second Year.—Chemistry Lectures, Junior* and Senior classes. Chemical Laboratory, three days per week. Technological Chemistry Lectures. Experimental Physics or Mineralogy Lectures and Practical Courses. German or French. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Third Year.—Chemistry Lectures, Senior* classes. Organic Chemistry Lectures. Chemical Philosophy. Chemical Laboratory, three days per week. Technological Chemistry Lectures (second course). Physical

Laboratory, 1 day per week, or Advanced Mineralogy Lectures and Practical Course. Mechanical Drawing, Practical (evening class).

Fourth Year.—Organic Chemistry Lectures.* Technological Chemistry Lectures (third and fourth courses). Chemical Laboratory, 4 days per week. Mechanical Drawing, Practical (evening class).

Fees.—Every student is required to pay on admission an entrance fee of £1 1s. and a library fee of 5s., and the fees for the classes for which he enters. As alternative courses are in some instances open to a student offering himself for the Victoria University Examinations, it is not practicable to give tabular statements of the fees for every combination of classes. Special prospectuses may be obtained at the office of the College.

The aggregate of the fees in each year will vary slightly according to the particular class selected in French or German, or to the choice made in respect of the other alternatives proposed.

When a student is excused a second attendance on any of the Chemistry Lecture Courses the fee will be reduced accordingly.

Certificates will be granted to students on the successful completion of this course. Attendance on the full course of four years is expected of candidates for the Certificate, but students may obtain exemption (on cause shown) from the first or the first and second year's courses. Students so excused will nevertheless be required to undergo examination in all the subjects specified.

The Certificate will state in which subjects the candidate has gained Honours, and in which he has merely satisfied the Examiners.

A number of important Exhibitions, &c., are available to students.

UNIVERSITY COLLEGE, NOTTINGHAM.

Professor of Chemistry—Frank Clowes, D.Sc. Lond., F.I.C., F.C.S.

Demonstrator—Mr. J. B. Coleman, F.C.S.

Lecturer on Dyeing.—Mr. R. L. Whiteley, F.C.S.

The Classes of the College are open to students of both sexes above sixteen years of age. In virtue of the affiliation of the College to Cambridge University a suitable course of study is recognised in lieu of part of the ordinary residence at Cambridge for those intending to take degrees at that University. Reference should be made to the College Prospectus for fuller information.

Lecture Courses.—A systematic course of day lectures is delivered on Tuesday and Friday afternoons at 4.30: the non-metals are treated of in the Autumn Term (October 4th to December 18th), the metals in the Spring Term (January 17th to April 2nd), and the carbon compounds in the Summer Term (April 25th to July 9th).

A course of evening lectures runs parallel with the day course, being delivered on Wednesday evenings at 8 o'clock.

A lecture class in connection with both courses meets on Wednesday evenings at 7 o'clock.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford: they may also obtain instruction in Chemistry for technical or other purposes.

Fees.—For the day lectures, £2 10s. for the session, and one guinea for a term; for evening lectures, 2s. 6d., or 5s. for lectures and classes per term.

There will also be Classes or Lectures on Chemical Philosophy and Calculations, the Chemistry of the Benzene Series and of Coal-Tar, the Chemistry of Dyeing and Bleaching, and the Chemistry of Brewing.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 1 and from 2.30 to 5.30, also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation

* Students who gain a place in the First or Second class in the annual examinations will be excused a second attendance on these classes.

and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, and other Manufacturing Processes. A set of ordinary apparatus and reagents and a private locker are supplied free of charge, for the safe keeping of which the Student is held responsible.

Fees.—For one term, £6; for the session, £15; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week; for evening students 10s. for one evening per week, and 20s. for two evenings per week.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrator of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry will be taught in the elementary and advanced stages, each of which commences at the beginning of the College Session in October. Fees for each Lecture Course, 2s. 6d.; for each Laboratory Course, 5s. Students joining these classes are expected to become candidates for the Government Examinations in May.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, F.C.S.

The Session will commence on Tuesday, October 5, 1886.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Friday, from 10 to 11 a.m. Fee, £3 13s. 6d.

Second Year's Course.—Chemistry of Metals. Tuesday and Thursday, from 10 to 11 a.m. £2 12s. 6d.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £1 11s. 6d. Chemical Philosophy, on Saturday at 10. Fee, £2 2s.

Analytical Chemistry.—Lecture course by Mr. O'Shea. Thursday, 11 to 12. Sessional fee, £1 11s. 6d.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £4 10s.; Nine, £6 10s.; Twelve, £8; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Monday, 8 to 9. Laboratory instruction, Monday and Wednesday, 6 to 9. Sessional Fee, one evening per week, £1 10s.; two, £3; or Lecture Class and Laboratory, on Monday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

Professor.—T. Carnelley, D.Sc., F.C.S.

Lecture Assistant.—Andrew Thomson, M.A., B.Sc.

The fourth session of the College will be opened on October 11th, 1886.

The Lectures and Laboratory practice in Chemistry are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the University of Edinburgh.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: Monday, Wednesday, and Friday, from 10 to 11 a.m.; fee, £2 2s.

Second year's lecture course: Tuesday, Thursday, and Saturday, from 9 to 10 a.m.; fee, £2 2s.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, and Agriculture. The courses are also suitable for students preparing for their medical and pharmaceutical examinations. A three months' course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction.

UNIVERSITY OF EDINBURGH.

Professor.—A. Crum Brown, F.R.S.E.

The Session will commence on October 19, 1886.

Two degrees in Science are conferred by the University of Edinburgh, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.). Both these degrees are conferred in Physical and Natural Science, in Public Health, and in Engineering.

Candidates for degrees in Physical and Natural Science must pass a preliminary examination in English, Latin, Arithmetic, the Elements of Mathematics, and the Elements of Mechanics, and in at least two of the following subjects:—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, and Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, including Comparative Anatomy, and Botany. The Second B.Sc. Examination the Higher Higher Mathematics, Natural Philosophy, Experimental Physics, Chemistry, Zoology, Botany, Physiology, and Geology.

The D.Sc. Examination embraces Mathematics, Applied

Mathematics, Experimental Physics, Practical Astronomy, Chemistry, Zoology and Comparative Anatomy, Animal Physiology, Botany, and Geology, including Palæontology and Mineralogy.

ANDERSON'S COLLEGE, GLASGOW.

Professor of Chemistry.—William Dittmar, F.R.S.

Chief Assistant.—John M'Arthur.

Laboratory Assistants.—Archibald Kling and Frank Lyall.

Junior Assistants.—James Robson and William Cullen.

A Course of 100 Experimental Lectures on Chemistry: Daily, Saturdays excepted, from 10.15 to 11.15, commencing on Wednesday, Oct. 27th. The Lectures up to the end of the year are devoted to an Elementary Exposition of the Philosophy and the Methods of the Science, as illustrated by the History of the Non-metallic Elements. The rest of the Session is divided between the Chemistry of the Metals and Organic Chemistry, select chapters. In addition to occasional extemporised examinations during class hours, five written examinations are held during the Session, on Saturdays from 10 to 1. Fee, £2 2s.

The Laboratory is open daily (Saturdays excepted) during the Winter Session from 10 to 5, during Summer from 9.30 to 5. Advanced students may obtain permission to work privately on Saturdays also until 1 p.m. The teaching is conducted on the tutorial system, each student working by himself, at a separate place, and on his own subject. Hence students of any grade of advancement may enter at any time, and the course of instruction can be adapted to the special requirements of the individual. Original research is not forgotten, but Mr. Dittmar makes it a strict rule not to use his students as his private assistants in connection with his own investigations, and to rather discourage original research with students who have not yet obtained a sufficient mastery of all the practically important methods of chemical analysis and of preparative chemistry. Fee per month, £2 2s.; due in advance. For any period of six months or more, if paid in advance, at the rate of £1 15s. per month. The fees include the use of all the ordinary reagents, and of the resources of the laboratory generally; but the student has to find his own small apparatus (test-tubes, beakers, &c.), and also a few of the more expensive reagents—*e.g.*, chloride of platinum, nitrate of silver, molybdate of ammonia.

Of the several duties which the prestige and traditions of this Chair impose upon its occupant, the first and foremost is to offer to young men, of even limited means, the opportunity of receiving a training in chemistry sufficient to prepare them fully for positions in chemical works, or as professional chemists.

A special Practical Class for Medical Students, meeting twice a week for two hours each time, is conducted during the Summer Session. Fee, including all expenses, £2 2s.

The Evening Department opens on the 2nd of October.

THE

"YOUNG" CHAIR OF TECHNICAL CHEMISTRY, ANDERSON'S COLLEGE.

Professor.—Edmund J. Mills, D.Sc. (Lond.), F.R.S.

Assistant.—Mr. C. Ellis.

This Chair has for its object the instruction of Students in Chemistry as applied to the various branches of industry in Chemical and other works, Metallurgy, Agriculture, &c.

LECTURES.—*Principal Course.*—A Course of Twenty-five Lectures will be delivered on Mondays, Tuesdays, and Wednesdays, at 10 a.m., commencing on November 1st. The Lectures will be illustrated with Experiments, Diagrams, and Models, as well as by the actual Inspection of Manufacturing Processes; and the progress of the Students will be tested by periodical Examinations. These Lectures will have reference to units of weight and measure, to the calculations necessitated by Chemical operations, and to the nature and laws both of the Chemical

process and its results, as illustrated in Chemical Technology. Fee for the Course, One Guinea.

Subsidiary Course.—A subsequent Course of Thirty Lectures will be delivered on Mondays, Tuesdays, and Wednesdays, at 10 a.m. This Course is more particularly intended for Dyers, Colour Manufacturers, Brewers and Distillers, Tar Rectifiers, Drysalters, and others interested in a knowledge of Technical Organic Chemistry. Fee for the Course, Two Guineas.

Evening Courses.—There will be a special evening course of twenty-five lectures on Oils, Paints, and Varnishes, commencing on October 18th.

There will be Practical Evening Classes in the following subjects:—Oils, Paints, and Varnishes; Bleaching, Dyeing, and Printing; Iron and Steel; Water Supply and Sewage.

Laboratories.—The Laboratories are open daily from 10 to 4, and on Saturday from 10 to 1 o'clock for practical working by the Students, under the superintendence of the Professor and his Assistants.

The Fee for attending the Laboratories is £20 per Session of Nine Months, £14 10s. for Six Months, £7 10s. for Three Months, or £2 10s. per month.

Students must have a fair acquaintance with elementary Chemistry.

The New Laboratory Buildings comprise four stories, with a lecture room in the rear, and are exclusively devoted to the purposes of this Chair.

The Trustees, having had under consideration the requirements of Inventors, Patentees, and others whose investigations require isolation and privacy, as well as professional advice, have included in the arrangements Five Private Laboratories. Electric Cable has been laid to these laboratories for the supply, if required, of adequate power.

Library.—A Students' Library Society was founded in 1875. Its objects are to provide a collection of standard chemical works, and to maintain a regular supply of chemical journals. A large number of works have already been purchased or bestowed, and nine journals are received. Annual subscription, Half-a-crown.

COLLEGE OF SCIENCE AND ARTS, GLASGOW.

Professor of Chemistry—A. Humboldt Sexton, F.C.S.

During the Session 1886-87 the following Courses of Lectures will be delivered:—

(1.) *Junior.*—A Course of about thirty Lectures, to be delivered on Tuesdays, at 4 o'clock, commencing October 5th. This Course will be of a very elementary character, and will be suited to the needs of those Students who only require a knowledge of the general principles of the Science. Fee, £1 1s.

(2.) *Senior.*—A Course of about ninety Lectures, to be delivered on Mondays, Wednesdays, and Fridays, at 4 o'clock, commencing on October 4th. This will be as complete a course of Elementary Chemistry as time will permit. About sixty Lectures will be devoted to Inorganic Chemistry and the remainder to the elements of Organic Chemistry. Fee, £2 2s.

(3.) A Course of about thirty Lectures on Metallurgy will be delivered on Tuesdays, at 2 o'clock, commencing October 5th. About ten Lectures will be devoted to a consideration of Fuels and Refractory Materials, and the remainder to the Metallurgy of Iron and Steel.

The Laboratories (which have recently been much enlarged and improved, and which now offer every facility for the study of Practical Chemistry) are open daily (except Saturdays), from 10 to 4. Every Student works independently, so that the special needs of each can be attended to. Special attention is given to the requirements of students who intend to devote themselves to Technical Chemistry as a profession. Fee, £12 for the entire Session (October 4th to May 31st), or £2 per month. As far as space will permit, Students will be allowed to work for shorter hours at proportionate fees.

The evening classes in Chemistry, Metallurgy, and Mineralogy commence on Monday, October 4th.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on November 2nd. A Competitive Examination, open to intending Students of Arts or Science, for twenty-five Entrance Bursaries, ranging in value from £39 to £5 each per annum, will be held on Friday and Saturday, October 29th and 30th. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the "University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, forming an introduction to the discussion of Chemical Theory; the Non-metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supplementary Lectures.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £5 5s. for the Session.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

The Session begins October 19th.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. The course of instruction is under the direction of the Professor of Chemistry, and of the Chemical Assistant. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—Maxwell Simpson, D.Sc., M.D., F.R.S., &c.

The Session begins October 19th. The Chemistry Classes are held on Mondays, Wednesdays, and Fridays.

The Course is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry and Crystallography, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Thence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course in Medicine, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, M.D. F.R.S.

Demonstrators.—Augustus E. Dixon, M.D., F.C.S.; William Early, F.I.C.; Robert E. Doran, F.C.S.; Charles E. Moore, A.B.

The general Laboratories now include working accommodation for 100 Students, and the Quantitative and Research Laboratories for about 40 Students. It is expected that the new Lecture Hall will be completed before the Courses of Lectures commence, on November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
STEPHEN'S GREEN, DUBLIN.*Professor of Practical and Theoretical Chemistry.*—W. Noel Hartley, F.C.S.

The Session commences on Monday, October 4, 1886.

The instruction comprises courses of Lectures on General, Applied, and Analytical Chemistry, and also a course of Lectures on Metallurgy.

The Chemical and Metallurgical Laboratories, under the direction of Mr. Hartley, are open every week-day during the Session, except Saturday. Instruction is given

in the different branches of Analytical Chemistry, including Assaying, and in the methods for performing Chemical Research. Fee, for the Session of nine months, £12; or for three months, £5; or for one month, £2.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are given to Students who have been a year in the College. There are also nine Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year.

A Diploma of Associate of the College is granted at the end of the three years' course.

Evening Classes.—Systematic Courses of Evening Lectures are given by most of the Professors throughout the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. This Institution is intended to afford such practical, scientific, and artistic instruction as shall qualify persons to become—(1) Technical teachers; (2) Mechanical, civil, and electrical engineers, architects, builders, and decorative artists; (3) Principals, superintendents, and managers of chemical and other manufacturing works. Prominent among the agencies adopted is a scheme of Technological Examinations, in connection with which a large number of classes have been instituted in the various manufacturing centres of the kingdom at which practical instruction is given in the application of Science and Art to different industries. The work done in these classes is inspected by the Institute, and, on the results of the annual examinations, certificates and prizes are granted. *Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The College fulfils the functions of a finishing technical school for those entering industrial life at a comparatively early age; of a supplemental school for those already engaged in the factory or workshop; and of a preparatory school for the Central Institution. It is under the general direction of the Principal or Superintendent of Studies. At the head of each Department is a Professor, who is assisted by one or more Demonstrators; and besides these there are Lecturers and Teachers for instruction in special subjects: Skilled Artizans are employed in the Workshops for the guidance of the Students. The Session is divided into three terms:—The Winter term commences on Tuesday, October 5th, and ends on December 22nd; the Spring term commences on Tuesday, January 18th, and ends on the 6th of April; the Summer term commences on the 26th of April and ends on July 15th, the evening classes terminating May 27th. An examination for the admission of Students will be held at the College at 10 o'clock on Wednesday, September 29th, 1886, and the work of the Session will commence on Tuesday, October 5th. The instruction consists of Day and Evening Classes and Laboratory Instruction.

CITY OF LONDON COLLEGE.—Evening Classes in Chemistry, Physics, Electricity, and other Science subjects.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—*Organic Chemistry*: A course of 30 Lectures, beginning on October 5th, at 7 p.m., by Mr. H. Chapman Jones, F.C.S. A supplementary Course of about twelve lectures for more advanced students begins in January. Laboratory work and Analysis on Tuesdays, from 6 to 8 p.m. Special facilities are provided for students preparing for the Second B.Sc.

(London) Practical Chemistry Examination. *Inorganic Chemistry*: A course of Thirty lectures to Elementary Students, beginning on October 5th, and a course on Chemistry and Analysis to Advanced Students, beginning on October 9th, by Mr. George Chaloner, F.C.S. Classes for Practical Chemistry and Analysis on Tuesday and Saturday evenings, beginning on October 5th.

CRYSTAL PALACE COMPANY'S SCHOOL OF ART, SCIENCE, AND LITERATURE. SCHOOL OF PRACTICAL ENGINEERING. *Principal*—Mr. J. W. Wilson, Memb. Inst. C.E.—This school was established with the purpose of affording to Students of Civil or of Mechanical Engineering the advantage of thorough practical instruction in the rudiments of either profession, and in the manipulation of materials. The leading object is to prepare Students, by systematic practical instruction, for professional articles, so that on entering an Engineer's office or works the pupil may at once be useful to his Principal, and enabled to take advantage of the opportunities for learning open to him, because he has mastered the elementary details of the profession. The school is also available for Students already articulated, who desire instruction in either the offices or shops. The Colonial Section is designed particularly for gentlemen who are going to the Colonies or abroad, as explorers or settlers. The object proposed is to afford them so much practical knowledge of scientific and mechanical work and expedients as shall enable them best to utilise the means at their disposal, especially when entirely dependent on their own resources.

SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN, 17, Bloomsbury Square.—The school opens on Friday, the 1st of October. Lectures on Chemistry and Physics, by Prof. Wyndham Dunstan, on Monday, Tuesday, and Wednesdays, at 9 a.m. The Laboratories for Practical Instruction in Chemistry as applied to Pharmacy, &c., under the direction of Prof. Attfield, assisted by Mr. F. W. Short, and Mr. Eastes, will be open daily at 10 a.m. throughout the Session. They are fitted up with every convenience for the study of the principles of Chemistry by personal experiment. They are specially designed for the student of Pharmacy, but are equally well adapted for the acquirement of a knowledge of Chemistry in its application to Medicine, Manufactures, Analysis, or Original Research. There is no general class for simultaneous instruction, each student following an independent course of study always determined by his previous knowledge; pupils can therefore enter for any period at any date. Fees for the Lectures, One Course, £3 3s.; an entire Session—Two Courses, £4 4s.; Perpetual Admission, £5 5s.; for Practical Chemistry, 10 months, 12 to 25 guineas, according to hours of attendance. *Council Prizes.*—At the end of each of the five months Courses of Lectures on Chemistry and Physics, and Botany and Materia Medica, a Bronze Medal and Certificates of Merit, and at the close of the Session (ten months) a Silver Medal and Certificates of Honour and Merit, are offered for competition by the Council. In the Class of Practical Chemistry, a Silver Medal, two Bronze Medals, and Certificates of Honour and Merit, offered by the Council, are competed for at the end of the Session.

NEW CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., M.P.S., and Mr. J. F. Burnett, F.C.S., M.P.S. In addition to the usual Chemical studies, Special Instruction Classes are held for Students of Medicine.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road.—Dr. John Muter, F.C.S. Daily, at 9 a.m. Lectures on Theoretical Chemistry, and Junior and Senior Course of Practical Chemistry.

SOUTH WEST LONDON CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 183, King's Road, Chelsea.—Special Classes for Students of Medicine. Mr. W. H. Martin.

ST. JOHN'S TRAINING COLLEGE, Battersea.—Both Theoretical and Practical Chemistry form part of the curriculum of the College.

ONSLow COLLEGE OF SCIENCE, 183, Kings Road, Chelsea, S.W.—Lectures and Laboratory instruction in Chemistry and Pharmacy. Special Evening Classes in Inorganic and Organic Chemistry, &c. The Chemical and Metallurgical Laboratories are open every day and evening for practical work. Principal, Mr. W. H. Martin.

CANNING TOWN AND PLAISTOW SCIENCE SCHOOLS, North Hallsville Board Schools, Canning Town.—Science Classes. Teachers, Mr. C. S. Dawson and Mr. F. R. Holloman.

ROYAL VICTORIA HALL, Waterloo Bridge Road, S.E.—Science and Technical Classes, Session 1886-87. Lectures will be given, commencing October 1st (with the exception of Chemistry Course, first Lecture November 3rd), in the following subjects:—Electricity and Magnetism, L. H. Owen, Esq.; Animal Physiology, Dr. Drew, B.Sc.; Inorganic Chemistry, W. Popplewell Bloxam, Esq., F.C.S. Classes are also held in Mathematics, Plane and Solid Geometry, Machine Construction and Drawing, Political Economy and Commercial Arithmetic. The instruction given is suited to artizans and practical men, and is chiefly in connection with the Science and Art Department, South Kensington.

BIRMINGHAM.—QUEEN'S COLLEGE.—In connection with this College the Chemistry Lectures are given at Mason Science College, by Prof. W. A. Tilden.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

DERBY CENTRAL SCHOOL OF SCIENCE.—Evening Lectures and Practical Laboratory Instruction, commencing September 24. Physics and Mathematics—H. Barfield, D.Sc. Chemistry—Mr. Small, B.Sc.

COLLEGE OF CHEMISTRY, ROYAL INSTITUTION, HULL. Professor, G. Carr Robinson, F.R.S.E., F.I.C., F.C.S. Lectures on Inorganic and Organic Chemistry and on the Manufacture of Oils, Colours, and Varnishes are given during the Winter months. Winter Session begins first week in October.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus. Fee: Fifty guineas per annum, with extra fee according to circumstances for the special course.

LEEDS SCHOOL OF MEDICINE.—Prof. Smithells.

SCHOOL OF SCIENCE OF THE CITY AND COUNTY OF LINCOLN.—Head-Master and Professor of Chemistry, Dr. A. B. Griffiths, F.R.S. (Edin.) F.C.S., &c. This new School of Chemistry and Science generally will be opened to the public on Monday, September 27th, 1886. The Chemical Laboratory is fitted with every appliance, apparatus, &c., essential for furnishing a well-appointed Laboratory. The Chemical Lecture Theatre is capable of holding 300 Students. Day Lectures on Advanced Inorganic and Organic Chemistry will be given by Dr. Griffiths during the Session. These Lectures will meet the requirements of the B.Sc. (Hon.) and M.B. Examinations of London University, &c. Mr. J. W. Horton, F.R.M.S. (Demonstrator on Chemistry) will give Junior Lecture Courses on Inorganic Chemistry, and also Lectures on Technical Chemistry. There will be Courses of Lectures on Agricultural Chemistry with Laboratory Practice, by Mr. Harris, superintended by Dr. Griffiths. Lectures on the higher Mathematics will be given by the Rev. Chancellor Leeke, M.A. (2nd Wrangler), and the Rev. W. W. Fowler, M.A., F.L.S. Dr. A. B. Griffiths will Lecture on Biology (including Animal Types,

Anatomy, Physiology, and Botany). The last two Courses will meet the requirements of London University, Scholarships and Exhibitions at Oxford and Cambridge Universities, &c. Dr. Griffiths will give an opening Lecture on his "Researches in Agricultural Chemistry," on Monday evening, September 27th. Syllabuses containing full particulars may be obtained at the School, or from Dr. Cant, Secretary, Silver Street, Lincoln.

THE TECHNICAL SCHOOL, MANCHESTER.—Lecturers on Chemistry, Physics, and Chemical Technology, H. Lloyd Snape, B.Sc. (Lond.), E. L. Rhead, Ernest Bentz, G. H. Hurst. The day classes commenced on August 31st, 1886, and the evening classes will commence on September 27th, 1886. First year: Lectures upon the Chemistry of the Non-metallic Elements, and of the more commonly-occurring Metals. Second year: Lectures upon the Purer Metals, Organic Chemistry, and Chemical Philosophy. In the Laboratories instruction is given in Qualitative and Quantitative Analysis. Practical classes are also held in the Metallurgical and Dyeing Laboratories. Technical Students have opportunity to attend, and are urged to join classes in mechanical drawing, and to take practical manual exercise in wood and metal working. Special practical work in any branch of Chemical Technology, or in preparation for University Examinations, will be arranged to suit individual Students. The evening Courses of instruction are especially designed to meet the wants of those already engaged in various industries. A syllabus, containing full particulars as to hours, fees, &c., may be obtained from Mr. J. H. Reynolds, The Technical School, Manchester.

SCHOOL OF SCIENCE AND ART, NEWCASTLE-ON-TYNE.—Chemistry and Metallurgy, Mr. P. Hawkrige, B.A.

QUEENWOOD COLLEGE, near Stockbridge, Hants.—Mr. M. Whitley Williams, F.C.S. Lectures on Inorganic Chemistry and Physics and Laboratory Instruction.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

UNIVERSITY OF ABERDEEN.—Mr. J. S. Brazier, F.C.S.

SCHOOL OF MEDICINE, SURGEON'S HALL, EDINBURGH.—Dr. Stevenson Macadam, F.R.S.E., Mr. Falconer King, Mr. Ivison Macadam, and Mr. Drinkwater.

EDINBURGH SCHOOL OF PHARMACY AND CHEMISTRY.—The instruction qualifies for graduation in Medicine and Science in the University of Edinburgh and other Examining Boards. Secretary, Mr. R. Urquhart.

EDINBURGH SCHOOL OF MEDICINE, 41, Chambers St.—Dr. Drinkwater, F.C.S.—The instruction here qualifies for all Medical Boards, Edinburgh University, London University, &c. Day and Evening Classes.

MINTO HOUSE MEDICAL SCHOOL, CHAMBERS STREET, EDINBURGH.—Mr. J. Falconer King, F.I.C., F.C.S. Lectures and Classes.

NEW VETERINARY COLLEGE, LEITH WALK, EDINBURGH.—Professor Ivison Macadam.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

SCHOOL OF CHEMISTRY, 138, Bath Street, Glasgow.—Dr. Wallace, Mr. Tatlock, and Dr. Clark. Day and Evening Classes.

CHEMICAL LABORATORY, 180, West Regent Street, Glasgow.—Dr. Milne. Day and Evening Classes.

QUEEN'S COLLEGE, GALWAY.—Dr. T. H. Rowney.

ROYAL COLLEGE OF SURGEONS IN IRELAND.—Sir Charles Cameron, F.I.C. The Laboratories of the College are provided with every appliance for the study of Chemistry, especially in its application to Medicine, Hygiene, and Pharmacy.

DUBLIN, CARMICHAEL COLLEGE OF MEDICINE.—Dr. C. R. C. Tichborne.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

DUBLIN, DR. STEEVENS'S HOSPITAL AND MEDICAL COLLEGE.—Mr. McHugh.

THE CHEMICAL NEWS.

VOL. LIV. No. 1400.

ON THE FRACTIONATION OF YTTRIA.*

By WILLIAM CROOKES, F.R.S., V.P.C.S.

HAVING already explained the methods of chemical fractionation, it may be useful now to describe some of the results yielded by an extended perseverance in these operations.

I must, in the first place, explain that my work has been confined to a limited and very rare group of bodies—the earthy bases contained in such minerals as samarskite, gadolinite, &c. These have been repeatedly put through the fractionation mill by other chemists, but the results have been most unsatisfactory and contradictory, no sufficiently good test being known whereby the singleness of any earth got out by fractionation could be decided, except the somewhat untrustworthy one of the atomic weight. I say *untrustworthy*, because it is now known that fractionation, unless it is pushed far beyond the point to which some Continental chemists have even carried it, is quite as liable to give *mixtures* which refuse to split up under further treatment of the same kind, as it is to yield a chemically simple body. This I have fully gone into in my paper “On the Methods of Chemical Fractionation.” The unsatisfactory nature of fractionation work may be seen from expressions used, in private letters to me, by some of the eminent chemists who have almost made this method their own. One writes—“It is very tiresome working with the rare earths, as we never can be sure when we have got a definite result. There will never be an end to their history. I am very tired of it, and am much inclined to give it up.” Another writes—“Unfortunately I commenced my researches on the rare earths with too little material, and I have not had the courage, at my age, to re-commence the work on more abundant material. The further I advance in my work the more I am convinced that no known method permits of the complete separation of these different earths one from the other.” A third writes—“One loses so much material in the separations that it appears to me scarcely possible, with the material available, to arrive at a successful solution of the question.” I could multiply similar quotations, all breathing the same almost despairing spirit.

It would certainly not have been prudent on my part to invite a time-honoured comparison, and “rush in” where so many eminent men “fear to tread,” were it not that good fortune had placed in my hands a physical test for these obscure molecular groupings which is of the most exquisite sensitiveness. I refer to what I have for shortness called the Radiant-Matter test.

It is well known that a limited group of these rare earths, when phosphoresced *in vacuo*, yield discontinuous spectra. The method adopted to bring out the spectra is to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness. It is then put into a radiant-matter tube of the form shown in Fig 1, and the induction spark is passed through it after the exhaustion has been pushed to the required degree. The phosphorescence occurs beneath the negative pole. As each gaseous molecule, carrying its charge of negative electricity with it, strikes the earthy sulphate, it has a tendency to part with its charge, provided it finds a body ready to take up the electricity; otherwise it retains its charge. Bodies like yttrium sulphate, &c., easily take the

electric charge, and under the stimulus phosphoresce, emitting light whose waves tend to collect round definite centres of length. The phosphorescent light which the discharge evokes is best seen in a spectroscope of low dispersion, and with not too narrow a slit. In appearance the bands are more analogous to the absorption bands seen in solutions of didymium than to the lines given by spark spectra. Examined with a high magnifying power all appearance of sharpness generally disappears: the scale measurements must therefore be looked upon as approximate only; the centre of each band may be taken as accurately determined within the unavoidable errors of experiment, but it is impossible to define their edges with much precision. The bands are seen much sharper when the current first passes than after the current has been passing for some time and the earth has become hot. On cooling the sharpness of the bands reappears.

As a general rule the purer the earth the sharper the band, and when impurities are removed to the utmost extent, the sharpness is such as to deserve the name of a line. This may be illustrated by mixing together yttria and lime. Lime phosphoresces with a continuous and yttria with a discontinuous spectrum. Mixed together, the phosphorescing energy of the lime does not spend itself over the whole spectrum but concentrates itself in greatly reinforcing the yttria bands. A molecule of yttria vibrating with a definite wave-length gives a nearly sharp line, but the molecule of lime with which it is weighted has no special tendency to vibrate to one wave-length more than another. The yttria induces

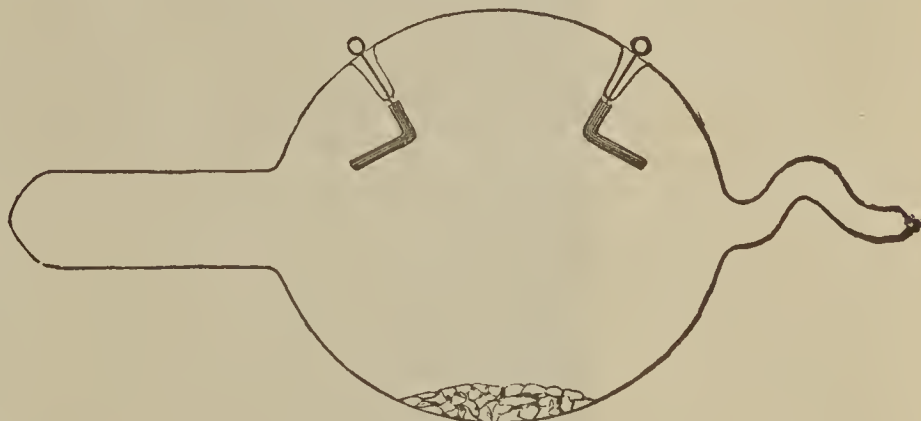


FIG. 1.

the right vibration in the adjacent molecule of lime; but this lime, once set in vibration, cannot confine itself to the exact wave-length required, and overflows a little on each side, and the result is a widening and blurring of the bands, becoming greater in amount as the extraneous earth increases in quantity.

To this rule one exception occurs. The body which I have named Sδ, or 609, is remarkable for the great sharpness of its phosphorescent line, and I have noticed scarcely any variation in its sharpness, however large the bulk of extraneous earth associated with it. This line, however, is sharper and brighter when the current is first turned on than it is after the earth has been phosphorescing for a minute or so.

In the Bakerian lecture on yttrium delivered before the Royal Society,* I described the phosphorescent spectrum given by this element, and in the address which I have had the honour of delivering before this section I gave a drawing of the spectrum of yttrium, together with a sketch of the train of reasoning by which I had been led to the opinion that excessive and systematic fractionation had split up this stable molecular group into its components, distributing its atoms into several groups, with different phosphorescent spectra.

No longer than twelve months ago the name yttria conveyed a perfectly definite meaning to all chemists. It meant the oxide of the elementary body yttrium. I have in my possession specimens of yttria from M. de Marignac (considered by him to be purer than any chemist had

* Read before the British Association, Birmingham Meeting, Section B.

* *Phil. Trans.*, Part 3, 1883.

hitherto obtained), from M. Clève (called by him "purissimum"), from M. de Boisbaudran (a sample of which is described by this eminent chemist as "scarcely soiled by traces of other earths"), and also many specimens prepared by myself at different times and purified up to the highest degree known at the time of preparation. Practically these earths are all the same thing, and up to a year ago every living chemist would have described them as identical, *i.e.*, as the oxide of the element yttrium. They are almost indistinguishable one from the other both physically and chemically, and they give the phosphorescent spectra *in vacuo* with extraordinary brilliancy. This is what I formerly called yttria, and have more recently called *old* yttria. Now these constituents of old yttrium are not *impurities* in yttrium any more than praseodymium and neodymium (assuming them really to be elementary) would be impurities in didymium. They constitute a veritable splitting up of the yttrium molecule into its constituents.

The plan adopted in the fractionation of yttria does not differ in principle from the methods described in my former paper, "On the Methods of Chemical Fractionation."

trate at the foot of the diagram (Fig. 2), where I give the spectra of five components of yttrium.

The final result to which I have come is that there are certainly five, and probably eight, constituents into which yttrium may be split. Taking the constituents in order of approximate basicity (the chemical analogue of refrangibility) the lowest earthy constituent gives a deep blue band $G\alpha$ (λ 482); then there is a strong citron band $G\delta$ (λ 574), which has increased in sharpness till it deserves to be called a line; then come a close pair of greenish blue lines, $G\beta$ (λ 549 and λ 541, mean 545); then a red band, $G\epsilon$, (λ 619), then a deep red band, $G\eta$ (λ 647), next a yellow band, $G\epsilon$, (λ 597), then another green band, $G\gamma$, (λ 564); this (in samarskite and cerite yttria) is followed by the orange line $S\delta$ (λ 609). The samarium bands remain at the highest part of the series. These, I am satisfied, are also separable, although for the present I have scarcely touched them, having my hands fully occupied with the more easily resolvable earths. The yellow band, $G\epsilon$, and green band, $G\gamma$, may in fact be due to a splitting up of samarium.

Until we know more about these bodies I refrain

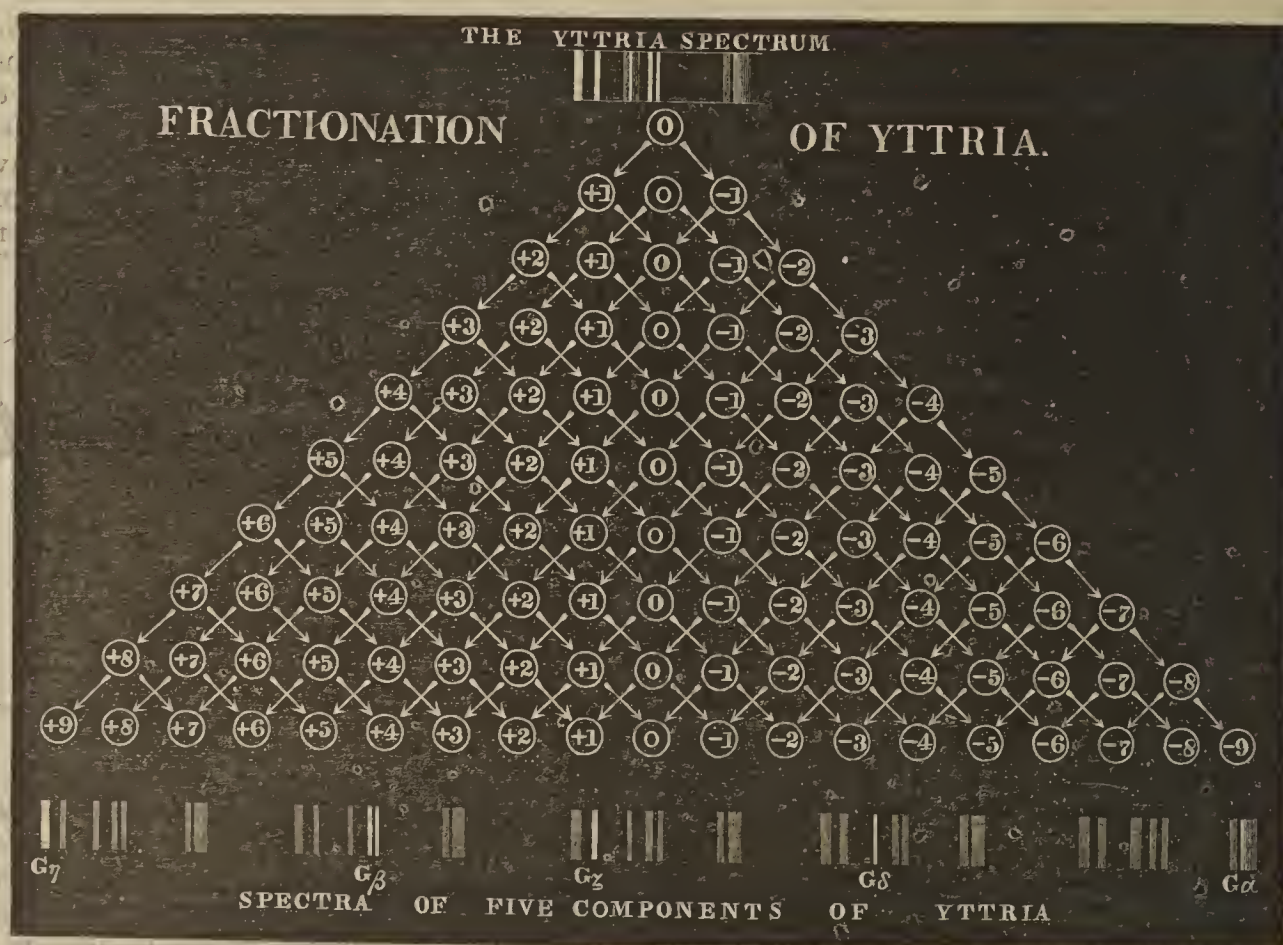


FIG. 2.

Dilute ammonia is added to a very dilute solution of the earth in only sufficient quantity to precipitate one half. After standing for several hours the precipitate is filtered. After each fractioning the filtrate is passed to the left and the precipitate to the right, and the operations are continued many thousand times.

The diagram (Fig. 2) shows the scheme clearly, with the direction the precipitates and solutions travel. Limited space, even on a large diagram, prevents me from giving more than a few operations, but they will be sufficient to satisfy you that enormous patience, a large amount of material, and a not insignificant number of bottles, are requisites for successful fractionation. Such proceedings are tedious enough even in their narration, but no mere words can enable any one to realise the wearisome character of these operations when repeated day by day, month after month, on long rows of Winchester quart bottles.

After a certain time, on examining the series of earths in the lowest line of bottles, their phosphorescent spectra are found to alter in the relative intensities of some of the lines, and ultimately different portions of the fractionated earths show spectra such as I have endeavoured to illus-

trate from naming them, but will designate them provisionally by the mean wave-length of the dominant band. If, however, for the sake of easier discussion among chemists a definite name is thought to be more convenient I will follow the plan frequently adopted in such cases, and provisionally name these bodies as shown in the Table. (See next page).

The initial letters S and G recall the origin of the earths respectively from Samarskite and Gadolinite.

Not only has yttrium been split up by subjection to fractionation, but samarium, as I have hinted above, is likely to prove equally unable to resist this operation. In the phosphorescent spectrum of samarium sulphate the line $S\delta$ (609) is one of the constituents. When yttria is added to samaria this line is developed in greater intensity, as yttria has the power of deadening the other bands of samarium, while it does not seem to affect the line $S\delta$. Several circumstances, however, tend to show that although line $S\delta$ accompanies samarium with the utmost pertinacity, it is not so integral a part of its spectrum as the other red, green, and orange lines. For instance, the chemical as well as physical behaviour of these line-forming bodies is different. On closely comparing the spectra of specimens of samaria

Position of lines in the spectrum.	Scale of spectroscope.	Mean wave-length of line or band.	$\frac{1}{\lambda^2}$	Provisional name.	Probability.
Bright lines in—					
Deep blue	8.931	482	4304	G α	New.
Greenish blue (mean of a close pair)	9.650	545	3367	G β	{ New, or the Z β of M. de Boisbaudran.
Green	9.812	564	3144	G γ	New.
Citron	9.890	574	3035	G δ	{ New, or the Z α of M. de Boisbaudran.
Yellow	10.050	597	2806	G ϵ	New.
Orange	10.129	609	2693	S δ	New.
Red.. .. .	10.185	619	2611	G ζ	New.
Deep red	10.338	647	2389	G η	New.

from different sources, line S δ varies much in intensity, in some cases being strong and in others almost absent; the addition of yttria is found greatly to deaden the red, orange, and green lines of samarium, while yttria has little or no effect on the line S δ ; again, a little lime entirely suppresses line S δ , while it brings out the samarium lines with increased vigour. Finally, attempts to separate line S δ from samarium and those portions of the samarskite earths in which it chiefly concentrates has resulted in sufficient success to show me that, given time enough and an almost inexhaustible supply of material, a separation would not be difficult. These facts, together with the peculiar behaviour of the lines G ϵ and G γ , strengthen my suspicion as to the resolvability of samarium.

Samaria giving the line S δ had been prepared from cerite and samarskite. Many observations had led me to think that the proportion of band-forming constituents varied slightly in the same earth from different minerals. Amongst others, gadolinite showed indications of such a differentiation, and therefore I continued the work on this mineral. Very few fractionations were necessary to show that the body giving line S δ was not present in the gadolinite earths; no admixtures of yttria and samaria from this source giving a trace of it. It follows therefore that the body whose phosphorescent spectrum gives line S δ occurs in samarskite and cerite, but not in gadolinite.

It now became an interesting enquiry whether all these constituents of yttrium were united together in exactly the same proportion in every case. A glance at the diagram before you will show that yttrias from different sources, although they may be alike as far as our coarser chemical tests are concerned, are not built up exactly in the same manner. Thus, when the samarskite yttrium was forming, all the constituent molecules—which I have provisionally named G α , G β , G γ , G δ , G ϵ , G ζ , G η , and S δ —condensed together in fair proportion. In gadolinite yttrium the constituents G β and G δ are plentiful, G ζ is very deficient, S δ is absent, and the others occur in moderate quantities. In the yttrium from xenotime G δ is most plentiful, G β occurs in smaller proportion, G ζ is all but absent, and S δ is quite absent. Yttrium from monazite contains G β and G δ , with a fair proportion of the other constituents, G β is plentiful and the red is good. Yttrium from fluocerite is very similar to that from monazite, but G α is weaker. Yttrium from hielmite is very rich in G δ , has a fair quantity of G α and G β , less of G γ , no S δ , and only a very faint trace of G η . Yttrium from euxenite is almost identical with that from hielmite. Yttrium from cerite contains most G ζ and C δ , less G α and G β , only a trace of G η , and a fair proportion of S δ .

I have already mentioned how the key to these explanations was gained by an examination of the phosphorescent spectrum of M. de Marignac's Y α (now called by him gadolinium).

Referring to the diagram it is seen that Y α is composed of the following band-forming bodies:—G β , S δ , G γ , together with a little samarium. Calling the samarium an impurity, it is thus seen that gadolinium is composed of at least three simpler bodies.

It is by a method of his own, differing from mine, that M. de Boisbaudran has obtained phosphorescent spectra of some of the rare earths. He takes the induction spark between the surface of a strong and acid solution of the metallic chloride, and a clean platinum wire a few millims. above it. The platinum wire is kept negative and the solution positive; it is then observed that in many cases a thin layer of fluorescent light is seen at the surface of the liquid. This layer gives a spectrum of nebulous bands. For the sake of brevity I will adopt M. de Boisbaudran's term, and call this process the *method of reversion* (the direction of the spark being reversed). As this method is entirely different to the one I adopt, it is not surprising that the results also are different. Experimenting in this way M. de Boisbaudran has obtained, among others, two bands (λ 573 and λ 543.2), which he considers are caused by two elements, named respectively Z α and Z β , and which he considers new, at all events if we except terbium and possibly the elements of what was formerly called holmium. His method fails to show any spectrum in solutions of yttria which by my method give the yttria bands with the greatest brilliancy; while conversely his method shows a fluorescent spectrum in solutions of earths separated as widely as possible from yttria, chemically as well as spectroscopically. My experiments on both these methods tend to the conclusion that our bands are not due to the same cause, although M. de Boisbaudran's experiments have led him to the opposite conclusion. The band of Z β (543) falls between the double green band G β and the band of Z α (573) would come very near the citron line G δ .

In the hands of a practised experimentalist like M. de Boisbaudran this method may give trustworthy indications, but I must confess that in my opinion the test is one beyond the range of practical analysis, owing to the enormous difficulty of getting the phenomena described by the discoverer. Unless the strength of spark, the concentration and acidity of solution, and the dispersion and magnifying power of the spectroscope bear a certain ratio one to the other, the observer is likely to fail in seeing a spectrum even in solutions of earths which contain considerable quantities of Z α and Z β . In my own case I not only have had the advantage of personal instruction in Paris from M. de Boisbaudran himself in the best method of getting these reversion spectra, but on returning to London I brought with me some of the identical earths which give these spectra at their best. In spite of these advantages I have sometimes experimented off and on for weeks without being able to see more than a feeble glimmer of the bands described by M. de Boisbaudran.

Again, when everything is most favourable and the reversion bands are at their strongest, they are but a faint and hazy shadow of the brilliant lines given by the bombardment process. M. de Boisbaudran, speaking of the relative sensitiveness of our two methods, says that the bombardment process *in vacuo* is incomparably more delicate than his reversion test, and I estimate the relative sensitiveness of the two methods to be in the proportion of about 1 to 100.

You have probably anticipated in your minds a question which is likely to occur at this point of the enquiry. If such results have been obtained by submitting yttrium to this novel method of analysis, what will be the result of fractionating some other reputed element?

Yttrium, as I have explained, is an exceedingly stable molecular group, capable of acting as an element, just as calcium, for instance, acts as an element: to split up yttrium requires not only enormous time and material, but the existence of a test by means of which the constituents of yttrium are capable of recognition. Had we tests as delicate for the constituent molecular groups of calcium, this also might be resolved into simpler groupings. It is one thing, however, to find out means of separating bodies which we know to be distinct and have colour or spectrum reactions to guide us at every step; it is quite another thing to separate colourless bodies which are almost identical both in chemical reaction and atomic weight, especially if we have no suspicion that the body we are dealing with is a mixture.

(I mention calcium because it is one of several other elements which I have put through the fractionation mill. Many hundred operations have given me just sufficient encouragement to make me wish I had time to push this work to the end).

One of the chief difficulties in the successful carrying out of an investigation in radiant matter spectroscopy is the extraordinary delicacy of the test. This extreme sensitiveness is a drawback rather than a help. To the inexperienced eye one part of yttrium in ten thousand gives as good an indication as one part in ten, and by far the greater part of the chemical work undertaken in my hunt for spectrum-forming elements was performed upon material which later knowledge shows did not contain sufficient to respond to any known chemical test. It is as if the element sodium were to occur in ponderable quantity only in a few rare minerals seldom seen out of the collector's cabinet. With only the yellow line to guide, and seeing the brilliancy with which an imponderable trace of sodium in a mineral declares its presence in the spectrum, I venture to think that a chemist would have about as stiff a hunt before he caught his yellow line as I have had to bring my orange and citron bands to earth.

Chemistry, except in few instances, as water-analysis and the detection of poisons, where necessity has stimulated minute research, takes little account of "traces" and when an analysis adds up to 99.999, the odd 0.001 per cent is conveniently put down to "impurities," "loss," or "errors of analysis." When, however, the 99.999 per cent constitutes the impurity and this exiguous 0.001 is the precious material to be extracted, and when, moreover, its chemistry is absolutely unknown, the difficulties of the problem become enormously enhanced. Insolubility as ordinarily understood is a fiction, and separation by precipitants is nearly impossible. A new chemistry has to be slowly built up, taking for data uncertain and deceptive indications, marred by the interfering power of mass in withdrawing soluble salts from a solution, and the solubility of nearly all precipitates when present in traces in water or in ammoniacal salts. What is here meant by "traces" will be better understood if I give an instance. After fifteen months' work I obtained the earth yttria in a state which most chemists would call absolutely pure, for it contained not more than one part of impurity (samaria) in two hundred and fifty thousand parts of yttria. But this one part in a quarter of a million profoundly altered the character of yttria from a radiant-matter-spectroscopic point of view, and the persistence of this very minute quantity of interfering impurity entailed another ten months' extra labour to eliminate these final "traces" and to ascertain the real reaction of yttria pure and simple.

The radiant-matter test applied to these phosphorescing bodies proves itself to be every day more and more valuable, and one of the most far-searching and trustworthy tools ever placed in the hands of the experimental chemist. It is an exquisitely delicate test capable of

being applied to bodies which have been approximately separated, but not yet completely isolated, by chemical means; its delicacy is unsurpassed even in the region of spectrum analysis; its economy is great, inasmuch as the test involves no destruction of material, and its convenience is such that any given specimen is always available for future reference. Likewise, the quantity of material is limited solely by the power of the human eye to see the body under examination. Beyond all these excellences is its trustworthiness. I should perhaps exceed the legitimate inference from experience were I to claim that this test is infallible; but this I may say—during the five years in which the test has been in daily use in my laboratory, I never once have been led to view its indications with suspicion. Anomalies and apparent contradictions have cropped up in plenty; but a little more experiment has always shown that the anomalies were but finger-posts pointing to fresh paths of discovery, and the contradictions were due to my own erroneous interpretation of the facts before me.

NEW COLORIMETRICAL ESTIMATION OF SULPHUR IN IRON.

By J. WIBORGH.*

THE colorimetical method of determining the amount of sulphur in iron which Prof. v. Eggertz worked out and published in 1860, in the *Jern Kontorets Annaler*, has been and still is indisputably of great utility to the Swedish iron manufacture. The method since then is in general use in our iron-works, and has incited me to proceed in the same direction. I have sought to perfect such a colorimetical process as would be applicable also for greater amounts of sulphur than that for which the Eggertz method is intended. This new colorimetical sulphur test will, I hope, fulfil the demands that in general may be put upon the practical requirements intended in the method; namely, it is quick and easy to execute, also it has sufficient accuracy to give the amount of sulphur, whether in cast-iron, steel, or wrought-iron. I proceed to a description of the method.

Basis of the Method.

Iron dissolves completely in diluted sulphuric acid or hydrochloric acid, and the gases evolved—hydrogen, carburetted hydrogen, and sulphuretted hydrogen—pass through a cloth impregnated with a metallic salt, and through the action of sulphuretted hydrogen a metallic sulphide is formed, which colours the cloth. From the intensity of the colour afterwards the amount of sulphur in the iron is decided.

I proceed here upon the assumption that a given surface is always coloured equally strong by a fixed quantity of sulphur. But to obtain an equal quantity of sulphur from two specimens of iron which have unequal amounts of sulphur, evidently the amounts of iron weighed out must be inversely proportionate to the amounts of sulphur. Therefore a weight W of an iron with sulphur amount S gives the same colour as a weight W' of another iron with sulphur amount S' ; so must—

$$WS = W'S';$$

and as S' is the amount of sulphur sought—

$$S' = \frac{WS}{W'}.$$

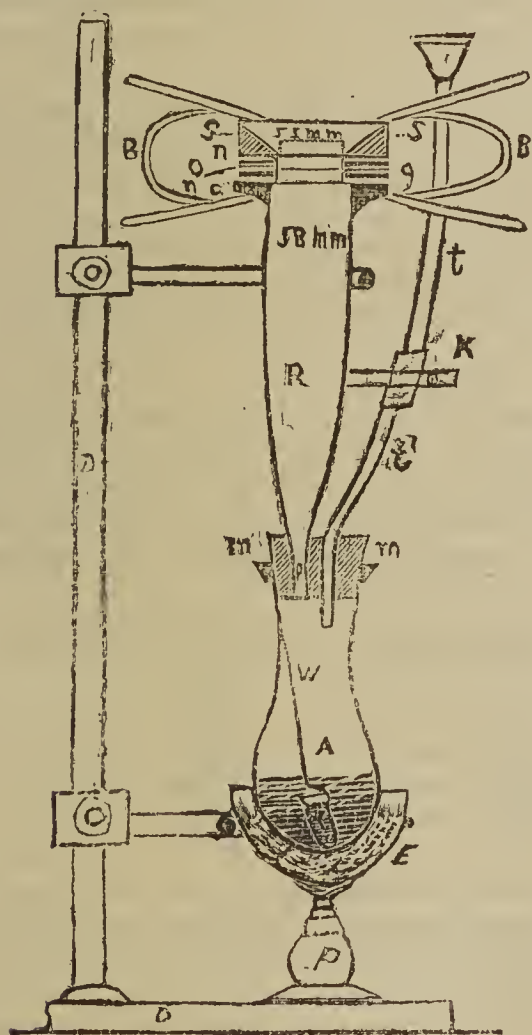
If you have thus an iron (normal iron) with the amount of sulphur accurately known, you can, by varying the amounts of it weighed out, produce a colour-series in which for every colour you know the product WS . This colour-series constitutes a scale with the aid of which

* Translated from the *Jern Kontorets Annaler*, 1886, p. 105, by J. Crum, Lowther Iron Works.

the unknown amount of sulphur S' in another iron can be determined by dividing the same colour's known product, WS, by the weight of the iron used for the assay.

The apparatus shown in the accompanying figure consists of a small boiling flask, A, provided with a close-fitting caoutchouc stopper, m, in which are placed a glass cylinder, R, with one end drawn out to a tube, P, and the other end having a flat polished flange, G, also a funnel tube, T, to introduce the acid. This latter consists properly of two, T and T', united with a caoutchouc tube, over which is placed a nipper tap, K, with a screw, so that the quantity of acid to be passed into the flask may be accurately regulated. Upon the cylinder flange is placed a caoutchouc ring, N, and upon this the prepared cloth, O. That the ring may close tightly against the flange and cloth, lay upon the cloth another caoutchouc ring, N', of the same size as the former, and outermost a wooden ring, S, which is pressed against the flange by the spring B.

These caoutchouc rings ought to have a precise inside diameter, for upon the size depends how much of the surface of the cloth will be coloured; as shown by the drawing it is made less than the opening of the cylinder, because it is easier to obtain such rings of a precise size



than the glass cylinder. In the apparatus represented the diameter of the ring O is 55, and the opening of the cylinder 58 millimetres.

In order that no steam may condense upon the ring S, and run down to the cloth, it is best to make this ring of wood rather than of glass or metal, of the size and form shown in the drawing.

By the arrangement now described neither gas nor steam can come from the apparatus without first passing through the cloth.

To heat the flask to boiling it is placed upon a sand-bath, E, which rests upon the stand D, and is heated by means of a gas or spirit lamp, P.

Preparation of the Cloth.

In the beginning I used, instead of cloth, unglazed paper, such as filter-paper, but I soon found that cloth was much more serviceable. Such paper certainly permits steam and gas to pass, but it is tender, and easily breaks asunder with the least incaution while boiling.

The cloth used is common, fine, white cotton calico. Linen is less suitable, for it is thin, and therefore does not absorb so easily all the sulphuretted hydrogen as evolved. The preparation of the cloth is simply to moisten it with a solution of a metal salt. For this may be employed either lead, silver, copper, cadmium, or antimony salts; but of all these I have found cadmium salts were for this purpose the most serviceable.

Silver and lead salts are certainly very sensitive to sulphuretted hydrogen; but the combinations of these metals with sulphur are black, and colour the cloth too strongly, so that it will be necessary to employ small weighings of the sample or extravagantly large apparatus.

Copper salts certainly give brownish and considerably softer colours, but, in consequence of the property of the sulphide to enter into variable combinations with the oxide, they are easily oxidised, and not permanent.

Antimony has few soluble salts, and besides in one case these are seen to be less sensitive to sulphuretted hydrogen; they are little fit for this purpose. A sufficiently dark colour is obtained by mixing the salts,—as, for example, cadmium and lead salts,—but has not led to any good results, as the colour comes out uneven, darker upon some places than upon others, so that the cloth has a more or less flannel-like aspect, varying between yellow and black.

For these reasons I have selected cadmium salt alone for the preparation of the cloth, and this the rather as the sulphur combination of cadmium is a particularly beautiful and constant yellow colour; also that the affinity of this metal for sulphur is so great that it surpasses that of lead.

When the cloth is impregnated with a mixture of cadmium and lead acetate, equal parts of each, and then exposed to a small quantity of sulphuretted hydrogen, the cloth at first will be almost exclusively yellow, and by the passage of more sulphuretted hydrogen it becomes dark, which shows well that the gas is sooner decomposed by cadmium than by lead. Again, concerning which of the cadmium salts ought to be selected for impregnation of the cloth it appears to be a matter of indifference which is employed, although the colour tint will be somewhat different as one or other salt is used.

Cadmium nitrate gives a singularly high and strikingly beautiful orange colour; the sulphate is somewhat weaker, with brownish yellow tint, while the chloride and acetate give lighter colours.

The colours occasioned by the varying amounts of sulphur may perhaps be most easily judged separately when the cloth is prepared with cadmium nitrate; but notwithstanding I have likewise used the acetate, because I think it likely that this salt, which has the weakest and most volatile acid, ought to give colours that would be least changeable, which property is of considerable weight.

In order that all the sulphuretted hydrogen may be absorbed by the cloth, it must contain a certain amount of cadmium salt in proportion to the largest quantity of sulphur which may possibly be present, otherwise a portion of the sulphuretted hydrogen will pass through the cloth, colouring yellow not only the under side, but also the upper side.

A solution of 5 grms. crystallised cadmium nitrate in 100 c.c. distilled water is of suitable strength.

Cloth of the proper fineness, prepared with such solution, allows not a trace of sulphuretted hydrogen to pass through, for the cloth was coloured only on the under side, and when double folds were used the upper had not the faintest colour.

The general influence of the degree of concentration of the solution is that the colours from strong solutions lie more upon the surface of the cloth, and that of weaker solutions it penetrates deeper into the cloth; and this causes a certain unevenness in the aspect of the colour, although the amount of sulphide of cadmium in both cases are alike. The influence of a smaller variation in the degree of concentration is not perceptible.

The cloth is prepared by cutting, on a round model, several folds to about 80 m.m. diameter. These are laid in the solution of cadmium acetate, care being taken that each circle is thoroughly saturated by the solution. After some minutes take out the pieces, and spread them out on a clean cloth until completely dried; then place them for safety in a suitable box.

The Colour Scale.

According to the quantity of sulphuretted hydrogen which reacts upon the prepared cloth, so is it covered with different amounts of cadmium sulphide, and receives a more or less yellow colour. The sensibility in this respect is so great that indeed 1000th part of a m.grm. of sulphur is able to communicate to the surface of a square centimetre of the white cloth a certainly weak, but yet very manifest, yellow colour. Increase successively the amount of sulphur by 1000th part of a m.grm. per square centimetre; you obtain by this small addition of sulphur from the first a clear distinction in the intensity of the colour; but in proportion as the strength of the colour increases with the augmented amounts of sulphur, the difference will be all the more difficult to observe. When the amount of sulphur increases to about 0.02 m.grm. per square c.m., the cloth is now strongly coloured, and to produce a manifestly distinct difference of colour intensity it requires two or three times greater excess of sulphur than with the lower colour estimations. Consequently you cannot with advantage make use of very strong colours, because the difficulty of their comparison is considerably increased.

In order to determine the amount of sulphur in an iron you must first have a colour series, or scale of colours, whereon every colour number represents a certain amount of sulphur per cent, presupposing that a certain quantity of iron has been weighed out for assay.

This colour series can be easily procured by the help of a normal iron in which the amount of sulphur has been determined beforehand with the greatest accuracy. How great the amount of sulphur this normal iron may contain is quite immaterial, but use the most trustworthy among the known methods of determining sulphur in iron by oxidation of the sulphur, and thereafter precipitating by chloride of barium. With small amounts of sulphur this is to a certain degree unsafe, so it is better to use for the scale an iron with a pretty high amount of sulphur, such as about 0.1 per cent, because the influence of a small error in this determination of the sulphur will be less.

If you have a known amount of sulphur S , also an iron of which 0.4 grm. is weighed out, and its amount of sulphur is S' , to obtain the same colour from both of the irons must—

$$W \times S = 0.4 \times S'$$

Or—

$$W = \frac{0.4 \times S'}{S}$$

In this formula place, instead of S' , the successive amounts of sulphur per cent, as 0.005, 0.01, 0.02, &c. As you know how much of the normal iron in every case ought to be weighed, so that you may have a series of colours that are entirely the same as those which shall be obtained if you had different irons with their respective amounts of sulphur and of each 0.4 grm. weighed; you get, in other words, a colour scale, where colours give directly the amount of sulphur the iron contains.

If you make up such a scale for the apparatus shown in the sketch, with the inner ring 55 m.m. diameter, you can under the supposition that 0.4 grm. has been weighed for testing: it is not desirable to go farther than this, so that the highest colour number corresponds to 0.1 per cent sulphur, because otherwise the colours will be too strong. Nevertheless you must not take between the high colour numbers a greater difference in the amount of sulphur than between the lower, if the different colour intensities shall be clearly separated from each other.

For example, you can allow the scale to be composed of seven colour numbers, taken thus:—

No. 1 corresponding to 0.005 per cent sulphur.

2	"	0.01	"	"
3	"	0.02	"	"
4	"	0.03	"	"
5	"	0.05	"	"
6	"	0.07	"	"
7	"	0.1	"	"

If thus 0.4 grm. iron is weighed for assay, one can, with the help of the above scale, determine the amount of sulphur up to 0.1 per cent. The accuracy wherewith the determinations is done are, for the lower of amounts of sulphur at least, to 0.005 per cent, and for higher 0.01 per cent, for the differences between the colours of the scale are here so great that one with the greatest ease can estimate a colour lying between two colour numbers.

The same scale may, however, be used to determine quickly whatever amount of sulphur is desired, if only the weight of iron used for assay be varied. It is obvious that absolutely the same colour which an iron gives from 0.4 grm. must be got from another iron with half as much sulphur, if 0.8 grm. has been weighed; and that, in general, if 0.4 n is weighed, the colour scale comes to represent sulphur amounts which are $\frac{1}{n}$ of those that answer to the weight 0.4 grm.

One ought therefore to use in general greater amounts for assay, when low amounts of sulphur shall be determined with great accuracy, also lesser quantities for high amounts of sulphur.

In the case of the colour coming out too strong—lying upon the margin or beyond the greatest amount of sulphur in the scale, the assay ought to be made with a lesser weight.

To avoid calculation one can, under every colour number, place not only the amount of sulphur which corresponds to that weighed out in making the scale, but also that which corresponds to some other weighings which possibly may occur. Note the following weighings, W , also the corresponding amounts of sulphur, S , per cent:—

0.8 gramme.	0.005 per cent.
0.4 "	0.01 "
0.2 "	0.02 "
0.1 "	0.04 "
0.08 "	0.05 "
0.04 "	0.1 "
0.02 "	0.2 "

With these different weighings are thus given the colour numbers of the amounts of sulphur from 0.005 per cent to 0.2 per cent.

Having by the above method prepared the different colour numbers which form the scale, they may be arranged in order upon small white drawing-paper, bound, and preserved in a suitable portfolio.

When cadmium acetate is used for the preparation of the cloth, the colour will be very constant. They have undergone no sensible change for several months, though preserved only in the above manner. One such scale ought to be made for every apparatus, and observe that the cloth used for the preparation of the scale must be the same sort as that afterwards used for testing.

Details of the Process.

Rinse every part of the apparatus with water, so that no acid remains from the former assay. The boiling-flask is half filled with distilled water; then fit the apparatus together and place on the sand-bath, which is heated by means of a gas- or spirit-lamp, so that the water in the flask comes to gentle boiling. While heating, weigh out the iron to be tested. This may certainly be in the form of small pieces, but, that the solution may not proceed too slowly, it is best if the iron is in the form of filings, turnings, or powder. Difficultly soluble iron, such

No.	Sorts of iron tested for sulphur by Wiborh's colorimetric method and by chloride of barium.	By Wiborh's method.	By wet method with chloride of barium.	
		Sulphur, p.c.	Sulphur, p.c.	Determined by—
1.	White charcoal cast-iron	0.005	0.005	A. Tamm.
2.	Spiegeleisen from Siegen, with 0.05 per cent copper ..	0.005	0.006	J. Wiborh.
3.	Bar iron, with 0.076 per cent arsenic	0.007	0.008	Y. Lagervall.
4.	Casting	0.0075	0.005	A. Tamm.
5.	Grey charcoal cast-iron	0.0075	0.005	A. Tamm.
6.	White	0.012	0.01	J. Wiborh.
7.	Casting	0.012	0.014	A. Tamm.
8.	Half-white charcoal cast-iron	0.018	0.018	J. Wiborh.
9.	Malleable casting	0.015	0.013	N. Lagerfelt.
10.	White charcoal cast-iron, with 0.071 per cent arsenic..	0.02	0.025	Y. Lagervall.
11.	White charcoal cast-iron	0.02	0.02	J. Wiborh.
12.	Malleable casting	0.023	0.024	E. v. Zweigbergk.
13.	White charcoal cast-iron	0.023	0.024	Y. Lagervall.
14.	"	0.025	0.022	A. Tamm.
15.	"	0.028	0.029	J. Wiborh.
16.	Cast-iron melted with copper, containing 1.55 p.c. Cu..	0.039	0.038	"
17.	Siemens-Martin iron	0.04	0.037	"
18.	"	0.05	0.047	"
19.	White charcoal cast-iron, with 0.015 per cent Cu..	0.06	0.061	"
20.	Steel	0.07	0.068	"
21.	Siemens-Martin iron	0.1	0.093	"
22.	Grey cast-iron	0.135	0.134	Y. Lagervall.
23.	Cannon cast-iron	0.15	0.145	J. Wiborh.
24.	White cast-iron from Hörde, with 1.88 per cent P..	0.21	0.19	E. Aquilon.
25.	Malleable casting	0.35	0.34	J. Jungner.
26.	White cast-iron from coke	0.45	0.46	J. Wiborh.
27.	"	0.7	0.66	P. G. Lidner.

as white iron,—high in silicon, phosphorus,—chrome iron, &c., ought always to be finely pulverised.

The weighed sample is brought, by means of a small funnel and hair-pencil, into the test-tube, *r*. This test-tube has the mouth widened. It is set in a loop made on the end of a platinum wire, *w*, which is bent over the edge of the test-tube, as shown in the figure, so that the platinum wire may not slip over the tube and rest on the bottom of the flask, which ought to be avoided, because the test-tube may take such a position that the access of the acid to the iron may be made difficult. The platinum with which the test-tube is thus fastened ought to be rather stiff—about 0.3 m.m. diameter.

After the water has boiled two minutes, and the air has been expelled, take out the stopper with the cylinder attached. The test-tube with the sample is lowered into the flask, where it rests on the bottom, held upright by the platinum wire.

Put the apparatus together again, and upon the cylinder flange lay the above-mentioned caoutchouc ring, 55 m.m. in diameter, and over it the prepared cloth; another caoutchouc ring, and lastly the wooden ring, all which are pressed together by the spring clamp.

As soon as the cloth is laid on screw up the clamp *k* on the funnel-tube, and steam must now pass through the cloth.

Partly to get the air as much as possible driven out of the apparatus, and partly to moisten the cloth, maintain the water in gentle boiling for about eight to ten minutes before any acid is introduced. Then fill the funnel-tube with diluted sulphuric acid (for example, $\frac{1}{4}$ volume sulphuric acid, 1.83 sp. gr., and $\frac{3}{4}$ volume water). Open carefully the screw-clamp *k*, and allow the acid to drop into the flask. For 0.4 gm. iron use about 10 c.c. dilute acid.

As soon as acid comes down the solution of the iron begins; steam and gases pass through the cloth, and in proportion as the solution proceeds, also according to the amount of sulphur in the iron, the under side of the cloth is more strongly coloured yellow.

After all the iron is dissolved, boil the solution further from five to ten minutes, to drive out the sulphuretted hydrogen which yet remains in the apparatus. Then open the spring clamp, remove the bottom ring, and lay

the cloth upon a piece of filter-paper to dry completely. It only remains now to determine the amount of sulphur by comparing the colour of the cloth with the colour scale.

That the liquid in the flask during the whole period is maintained at an even but *gentle boiling* is very essential for this process. The boiling ought to be so strong that the steam is always seen to pass through the cloth, but by no means so violent that the cloth becomes stretched by the boiling. For when it happens that the cloth, in consequence partly of this stretching and partly from the condensed steam, becomes more and more close, and takes a strongly convex form, then the pressure in the apparatus increases, so that on the introduction of the acid the gases formed rush through the funnel-tube. With cautious boiling one need never fear such occurring.

In order to avoid oxidation of the sulphuretted hydrogen formed during the solution of the iron, it is of importance that before the acid is introduced into the flask the air is as completely as possible expelled from the water and the apparatus, also that the boiling is so strong that plenty of steam always accompanies the gases which pass through the cloth.

The cloth in the assay ought to be coloured evenly, for if the colour is uneven it very considerably increases the difficulty of estimating the colour strength.

Whether the colour comes out even or not depends chiefly upon the construction of the glass cylinder. It ought to be so accurately made that the centre line of the tube coincides with that of the cylinder. Further, the tube ought to be short and of a conical form, 7 to 8 m.m. diameter at the lower end.

If the tube is too wide the cloth is always coloured unevenly; and again, if it is too small, drops of water condensed in the tube are cast up on the cloth, which give it a spotted aspect. The drawing represents the cylinder so set in the caoutchouc stopper that the mouth of the tube is even with the under side of the stopper; but it is still better to allow the end of the tube to be 5 to 10 m.m. under the stopper. It is certainly now more difficult for the water to leave the tube, and causes—especially at first, before the cylinder becomes warm—a weak bubbling; but this has no hurtful influence, but contributes to the more evenly colouration of the cloth.

Observe, further, that the glass cylinder is placed by the eye as vertical as possible, also that the apparatus is not placed in a draught.

The time required for a sample is half to three-quarters of an hour, according as the iron is more or less soluble.

This new method, in many special experiments, has given most satisfactory results, in that it is independent of the amounts of carbon and silicon in the iron, indicating high as well as low amounts of sulphur in iron, as seen in the accompanying Table with sulphur determinations in different sorts of iron. These have been performed by this method, and controlled by accurate estimations of the sulphur by the wet method. (See Table preceding page).

I have also tested if some impurities in iron—such as copper and arsenic—had any influence upon this method. For this purpose several sorts of iron containing copper and arsenic were specially selected from the collection of the Mining School; and in the Table it is found—

I. In the samples 2, 16, and 19 copper has no action; also—

II. In samples 3 and 10 the same is probably the case with arsenic, for the certainly somewhat large difference in the sulphur determination which occurs in sample 10 must be sought in other circumstances, as sample 3—even with its small amount of sulphur and high amount of arsenic—shows no noticeable difference.

The apparatus may be made of whatever size is wished, but in relation to use in Sweden it is seldom necessary to examine iron with a greater amount of sulphur than 0.1 per cent. I regard an apparatus with an inner ring of 55 m.m. as diameter of a suitable size. On the other hand, if one has in general to test iron with high amounts of sulphur, as cast-iron made with coke, &c., I would recommend that the apparatus be made somewhat larger.*

EMBOLITE: ITS COMPOSITION AND FORMULA.

By CUTHBERT WELCH.

(Concluded from p. 95.)

V. 3AgCl.2AgBr.

	A.	B.	C.	D.	Theory.
AgCl ..	52.793	52.8	53.2	53.4	53.378
AgBr ..	47.207	47.2	46.8	46.4	46.622
	100.000	100.0	100.0	99.8	100.000
Or,					
Ag ..	66.862	66.85	66.9	66.94	66.956
Br ..	20.088	20.09	19.9	19.82	19.839
Cl ..	13.050	13.06	13.2	13.18	13.205
	100.000	100.00	100.0	100.00	100.000

A. Plattner, from Colorado Mine, Copiapo, Chili. (*Poggendorff's Annalen*, lxxvii., 134).

B. Domeyko, from Chanarcillo, Chili. ("Elementos de Mineralogia," 1845, 203). Asparagus green.

C. Colonel P. Yorke, from Chanarcillo, Chili. (*Quarterly Journal of Chemical Society*, iv., 149, 1852).

D. F. Field, from Chanarcillo, Chili. (*Quarterly Journal of Chemical Society*, x., p. 239, 1858). Dark green.

VI. 5AgCl.2AgBr.

Domeyko, (*Annales des Mines*, (4), vi., p. 153, 1844), and ("Elementos de Mineralogia," 1845, p. 203). Colour pearly greyish green. From Chili. A. From Chanarcillo. B. From Quillota.

* Complete apparatus with colour scales and prepared cloth can be obtained either through the author or F. O. Söderberg, Mining School, Stockholm.

	A.	B.	Theory.
AgCl	65.6	66.4	65.615
AgBr	34.4	33.6	34.385
	100.0	100.0	100.000
Or,			
Ag	69.14	69.28	69.066
Br	14.63	14.30	14.632
Cl	16.23	16.42	16.302
	100.00	100.00	100.000

VII. 5AgCl.6AgBr.

Mr. J. M. H. Munro, from St Arnaud (*CHEMICAL NEWS*, liii., p. 99, 1886).

	Theory.
AgCl	39.276
AgBr	60.724
	100.000
Or,	
Ag	64.45
Br	25.84
Cl	9.70
	99.99
	100.000

VIII. 6AgCl.AgBr.

Domeyko, from Chanarcillo, Chili. (*Annales des Mines*, (4), vi., p. 153, 1844). Pearly greyish green.

	Theory.
AgCl	81.4
AgBr	18.6
	100.0
Or,	
Ag	71.94
Br	7.92
Cl	20.14
	100.00
	100.000

IX. 7AgCl.2AgBr.

Domeyko, from Chanarcillo, Chili. (*Annales des Mines*, (4) vi., p. 153, 1844).

	Theory.
AgCl	72.9
AgBr	27.1
	100.0
Or,	
Ag	70.44
Br	11.53
Cl	18.03
	100.00
	100.000

X. 7AgCl.5AgBr.

Domeyko, from Chanarcillo, Chili. (*Annales des Mines*, (4) vi., p. 153, 1844.) Asparagus green.

	Theory.
AgCl	51.0
AgBr	49.0
	100.0
Or,	
Ag	66.54
Br	20.85
Cl	12.61
	100.00
	100.000

Surely it cannot be contended that three substances possessing, respectively, 20.297, 43.288, and 82.078 per cent of AgCl are the same mineral with but an allowable variation in composition.

VERIFICATION OF THE CALCULATION OF
THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 102.)

XV. Relation between Silver and Bromide of Ammonium,
γ 51.

Bromide of ammonium.	Equivalent in silver.	Ag: NH ₄ Br = 100.
10.77165	11.85891	90.83169*
10.31995	11.36168	90.83121
20.43458	22.49766	90.82981 m
11.27594	12.41414	90.83144*
13.40256	14.75537	90.83173 M
24.36270	26.82197	90.83113
8.93490	9.83692	90.83025

Average 90.83104*

Log = 1.9582343

The bromide in the last determination was prepared by Deville.

All the samples of chloride and bromide of ammonium sublimed without leaving the least trace of any residue.

XVI. Syntheses of Nitrate of Silver, β 281.

Two series of syntheses have been effected. The silver used in the first series contained traces of silica, (α 237—251). I have, therefore, only calculated the two estimations published in 1865, which were carried out with infinite care. M. Stas considers these determinations to be absolutely irreconcilable with Prout's hypothesis, and he has suggested that a chemist of established scientific reputation should repeat this synthesis. Nobody having come forward in answer to his appeal, he himself repeated it in 1882 (β 305; γ 65).

* Ann. Chim. Phys., 6th Series, vol. vii., April, 1886.

The estimations of 1860 and 1865 are tolerably close; but still there remains an uncertainty of $\frac{1}{10000}$ as to the exact composition of nitrate of silver. In fact, nitrate of silver, dried at its melting-point, on being re-melted gives off some traces of acid vapours. Once melted it no longer loses weight, even when kept liquid in *vacuo* for fourteen hours (α 249).

During the years 1860 and 1865, M. Stas believed it more rational to consider the melted nitrate as the normal compound (α 251; β 286).

But in 1882, he seemed to lean towards the belief that the dried nitrate was more exact (γ, 62, 72, 73, 77). I admit my incompetence to decide this point, which has such a decided influence on the atomic weight of nitrogen. (See Table A).

M. Stas has also determined the relation between nitrate of silver and the chlorides of potassium and ammonium, (α 293—294).

The hygrometric property of the melted nitrate has caused an uncertainty of more than 1 m.grm. on a weight of 10 grms. to 30 grms. Further, the saline limit only has been determined, and the variation between the several results is greater than in the other estimations carried out by M. Stas.

I have, therefore, thought it necessary to eliminate these series of experiments, which would not help in determining the atomic weights founded on a surer basis.

XVII. Relation between the Chloride and the Nitrate of Potassium, β 244.

The weight in air is the only weight which is given with these salts. M. Stas has only applied the reduction for *vacuo* to the averages; he considers this correction to be = 0.003. To arrive at this figure, it is necessary to admit that the specific weight of the nitrate is 2.018 if that of the chloride is 1.950. (The weight of 1 litre of air is 1.28 gm.)

All the samples of chloride of potassium contained silica, which did not change in weight by the action of

TABLE A.

Silver.	Nitrate of Silver.		Ag: AgNO ₃ = 100	
	Dried at its Melting-point.	Melted.	Dried.	Melted.
136.2952	214.6600	214.6462?	157.4963 M	157.4862*
82.3231	129.6555	129.6420	157.4959* m	157.4795
			Average 157.4961*	157.4828*
			Log. = 2.1972699	2.1972333

TABLE B.

Chloride of Potassium.	Nitrate of Potassium.	KCl: KNO ₃ = 100 roughly.	Chloride produced.	Silica per 100,000.	Correction for Silica.	Relation corrected for Silica and for Vacuo.
50.7165	68.7938	135.6438	Nitre	5 to 6	0.0021	135.6429
80.2610	108.8665	135.6406*	Chloride of Potassium	5	0.0018	135.6394
72.1022	97.8050*	135.6478		5	0.0018	135.6466
50.2175	68.1200	135.6499	Chloroplatinate of Potassium	2 to 2.5	0.0009	135.6478 M
48.9274	66.3675*	135.6449		2 to 2.5	0.0009	135.6428
69.8836	94.7900	135.6398	Old figures	5	0.0018	135.6386 m
14.2578	19.3415	135.6556		?	?	

Average 135.6430
Log. = 2.1323974

TABLE C.

Chloride of Sodium.	Nitrate of Sodium.	NaCl: NO ₃ = 100 roughly.	Chloride produced.	Silica per 100,000	Correction for silica.	Relation corrected for Silica and for Vacuo.
120.0110	174.5590	145.4525	Carbonate	5	0.0023	145.4498 m
32.4837	47.2550	145.4730*	Chloroplatinate of Sodium	3.5	0.0016	145.4696 M
68.1295	99.1045	145.4649		4.?	0.0018	145.4617
47.9226	69.7075	145.4585		4.5	0.0020	145.4555

Average 145.4592
Log = 2.1627412

nitric acid. The amount of silica diminishes the relationship by 0.000356. (See Table B).

The last experiment was omitted in calculating the average.

XVIII. Relation between Chloride and Nitrate of Sodium, β 248.

The reduction for vacuo is, according to M. Stas, 0.005. As chloride of sodium has a specific weight of 1.145, that of the nitrate should be 2.276. The fifth experiment has been eliminated, because the glass retort used was not acid proof. (See Table C).

The second determination was made with the collaboration of Kekulé. In 1882 M. Stas showed preference for the three last experiments (γ 63).

XIX. Relation between Silver and Chloride of Lithium, β 268.

There were only a few experiments made with lithium, and, in spite of their agreement, M. Stas hesitates in saying that the atomic weight of lithium is not 7.00. The saline limit only was found.

Chloride of Lithium.	Equivalent in silver.	Ag: LiCl = 100.
7.88452	20.0335	39.3567 m
6.9210*	17.5843	39.3590*
10.96584	27.8597	39.3609 M

Average 39.3589*
Log. = 1.5950430

The chloride of lithium was weighed in vacuo, and contained absolutely no fixed residue.

XV. Relation between Chloride and Nitrate of Lithium, β 274.

Chloride of Lithium.	Nitrate of Lithium.	LiCl: LiNO ₃ = 100.
23.0260	37.43756	162.5882 m
30.8542	50.16835	162.5981*
34.1700	55.5605	162.6003* M

Average 162.5955
Log. = 2.2111085

The weights are already reduced for vacuo.

(To be continued.)

NOTICES OF BOOKS.

The Methods of Glass-Blowing. By W. A. SHENSTONE.
London: Rivingtons.

THE want of a practical treatise on glass-blowing has long been felt, and the work now before us satisfies this want in a very satisfactory manner.

Until within the last few years glass-blowing was generally looked upon as an art beyond the power of most students, skilful amateurs being regarded as something out of the common; while the glass-blowing trade was kept in the hands of a very few men, all known to each other, and who kept up the prices of even simple work to an almost prohibitive figure. But the law of supply and demand has once more asserted itself in a striking manner: the introduction of incandescent lamp-making has in a few years entirely altered this state of things, and it is now not an uncommon thing to see girls of 14 and 15 years of age turning out work which quite recently was looked upon as a creditable performance for a man of mature age. This result has been brought about by careful tuition, and a book such as this one will surely be of great value to those who have little or no opportunity of seeing the operations of glass working actually done.

The first chapter is devoted to a description of the

apparatus necessary, and the most convenient arrangement of the same. The different varieties of glass are next dealt with, and the characteristics of good glass are detailed.

The third and fourth chapters describe, step by step, the manner of making such apparatus as are generally used in chemical and physical laboratories, while the fifth and last chapter gives directions for calibrating vessels and etching on glass.

The only point to which we might take exception is the Appendix, which gives thirty-six diagrams said to represent the diameter and thickness of the tubes most frequently required, each pattern being designated by a number. In a somewhat extended experience we do not remember to have heard glass tube referred to by these or any other numbers, while, on the other hand, the sizes of tube made run so imperceptibly from one to the other that it would be difficult to say where to draw the line between one number and the next.

Report of Proceedings of the Michigan Board of Health Regular Meeting, July 13th, 1886.

AT this meeting Dr. Victor C. Vaughan, Professor of Physiological Chemistry in the University of Michigan, made an important communication concerning tyrotoxin. This is a very poisonous ptomaine, developed under certain circumstances in cheese and in milk. Its presence in cheese was recognised about a year ago, as reported in the *Zeitschrift für Physiolog. Chemie* (vol. x., Part 2), and the *Annual Report of the Michigan State Board of Health for 1885*.

A serious case of poisoning from ice-creams, which took place lately at Lawton, in the same State, has again called attention to the subject. Prof. Vaughan uses the following method for its isolation:—The coagulated milk was filtered through thick Swedish-paper. The filtrate, which was colourless and of a distinctly acid reaction, was rendered faintly alkaline with potassium hydrate and agitated with ether. The ethereal layer, after it has separated, is drawn off with a pipette, passed through a dry filter-paper to remove a suspended white flocculent substance, and allowed to evaporate spontaneously. If necessary the residue may be re-dissolved in water and again extracted with ether. On the evaporation of the ether the tyrotoxin is recognised by its crystalline appearance, its odour, and its action on the tongue.

Dr. B. C. Moffit, of Lawton, one of the sufferers from the ice-cream case, thus describes the symptoms observed:—“About two hours after eating the cream everyone was taken with severe vomiting and afterwards with purging. The vomit was of a soapy character. There was some griping of the stomach, with severe occipital head-ache, excruciating back-ache, and bone pains all over. Even after ten days the symptoms do not entirely disappear.” Dr. Vaughan experimented on himself with the pure poison, and experienced very similar results. The circumstances under which the poison is generated require further investigation.

The author suggests that “a little dried milk formed along the seam of a tin pail, or a rubber nipple, tube, or nursing-bottle not thoroughly cleansed, may be the means of generating, in a large quantity of milk, enough of the poison to render it highly harmful to children.”

Dr. Vaughan's paper and the cases which gave rise to it are very suggestive as regards the possible dangers of the street ice-cream trade.

The author has not yet obtained sufficient tyrotoxin for quantitative analysis.

Phosphorography applied to the Photography of the Invisible.—Ch. V. Zenger.—Images of a number of bodies can be obtained in the dark when, like calcium carbonate, paper, &c, they possess the property of slowly re-emitting the light which they have absorbed during insulation.—*Comptes Rendus*, Vol. ciii., No. 9.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 8, August 23, 1886.

On the Purple of the Solar Spectrum.—C. Kœchlin.
—This memoir will be inserted in full.

No. 9, August 30, 1886.

At the opening of the session the President formally conveyed to Prof. Chevreul the congratulations and good wishes of the Academy on the centenary of his birthday. Several foreign *savants* were officially present to join in the congratulations, to which the veteran chemist replied with profound emotion.

Atomic Weight of Germanium.—Lecoq de Boisbaudran.—The mean value found by Prof. Winkler from the determination of the chlorine in four specimens of germanic chloride is 72.32, which agrees well with the author's determinations, obtained on theoretical principles, and showing respectively 72.28, 72.32, and 72.27.

No. 10, September 6, 1886.

Fluorescence of the Compounds of Manganese, submitted to the Electric Effluve in a Vacuum.—Lecoq de Boisbaudran.—The fluorescences of the manganese compounds are remarkable from the variety and the brightness of their colours, and from their spectral resolution into a characteristic band, which varies in aspect and position with the nature of the manganiferous substance. Manganese sulphate alone (previously heated to dull redness according to the process devised by Mr. Crookes for the rare earths) does not fluoresce appreciably in a vacuum. Mn_3O_4 , derived from the ignited carbonate, gives nothing. Calcium sulphate alone (after ignition to dull redness) gives merely a faint fluorescence with a continuous spectrum; but if it contains a little manganese sulphate it is illuminated with a splendid green tint. A trace of manganese suffices to produce this fluorescence. With 1-100th of manganese sulphate the fluorescence is fine, and with 1-20th superb. The spectrum is continuous, but it contains neither the red nor the violet. It is a very broad band, beginning indistinctly about $\lambda=660$, having its maximum intensity about 540, and terminating vaguely between the blue and the violet. Calcium carbonate, not previously ignited, is scarcely illuminated at all in a vacuum. After strong ignition it yields a fluorescence generally of a violet blue at the points most directly exposed to the action of the electrode, violet at a little distance, and bluish green further off. The supposed pure calcium salts are rarely free from strontium, which gives a fine blue fluorescence. With the same calcium carbonate rendered slightly manganiferous we obtain, after strong ignition, a splendid orange-yellow fluorescence. The light is condensed in a brilliant band beginning vaguely about $\lambda=670$, having its maximum intensity about 589, the end of its chief luminosity about 553, and losing itself about 526. With 1-100th MnO the fluorescence is very fine, constituting a reaction still more sensitive than the green fluorescence of calcium sulphate with manganese sulphate. Magnesium sulphate alone, heated for a moment to dull redness, gives only a feeble greenish white fluorescence, but a little manganese sulphate enables it to fluoresce with a splendid redness. Zinc oxide, pure or manganiferous, ignited, gave no appreciable fluorescence. Zinc sulphate alone, after heating to dull redness, yielded merely a pale rose fluorescence with a continuous spectrum. But if it contains a little manganese sulphate there appears, after ignition, a splendid red fluorescence of a shade less inclining to orange than that of magnesium sulphate, with a little manganese sul-

phate. Analogous observations have been made with cadmium, strontium, lead, and glucinum sulphates, in all which cases a striking fluorescence was produced by the addition of a little manganese sulphate.

Moniteur Scientifique, Quesneville.
3rd Series, Vol. xvi., August, 1886.

Patents for Colouring-Matters granted at Berlin in March and April, 1886.—These comprise: Process for the preparation of new azo colouring-matters, yellow, red, and blue, by means of the bidiazo-derivatives of the ethers of the diamido-diphenols, of the phenols, or the amines.—F., No. 2585, Nov. 18, 1885.

Basic colouring-matters obtained by diazotising meta-nitraniline and combining these diazo-derivatives with meta-phenylene-diamine.—L., No. 3262, Aug. 4, 1885.

Preparation of blue sulphuretted colouring-matters.—R., No. 3467, Dec. 29, 1885.

Preparation of Aldehyds of the quinoleic series.—F., No. 2635, Dec. 28, 1885.

Preparation of blue rosanilines, soluble in water, by the action of aromatic diamines upon the rosanilines. Oxidation upon the fibre of the colours obtained with these new colouring-matters.—D., No. 2536, March 10, 1886.

Preparation of indulines soluble in water by the reaction of the aromatic diamines upon the amido-azo compounds. Oxidation of these colouring-matters upon the fibre.—D., No. 2535, March 10, 1886.

German Review.—G. Serracin.—A number of extracts from the *Berichte der Deutschen Chem. Gesellschaft*.

On Saccharine.—From the *Journal of the Society of Chemical Industry*.

Application of Electricity in Metallurgy.—M. Vedrinsky.—In this extensive memoir the author describes the electrolytic refining of copper, the Marchese electrolytic process, and the Cowles process for smelting metals by electricity.

Use of Explosive Matters for Working Engines.—M. Razeuvaieff.—The author undertakes to prove that engines fed with nitro-compounds can never compete economically with steam-engines.

New Contributions to the Determination of Tannins.—H. R. Procter, F.C.S.—From the *Journal of the Society of Chemical Industry*.

New Notes on the Methods of Examining Fixed Oils and on their Chemistry.—A. H. Allen.—From the *Journal of the Society of Chem. Industry*.

Manufacture of Toilet Soaps.—Dr. Alder Wright, F.R.S.—Also from an English source.

Documents on Quinine.—Dr. O. Hesse.—From the *Pharmaceutical Journal*.

Absorption of Potassium and Calcium Bicarbonates by the Rootlets of the Beet.—H. Leplay.—From the *Comptes Rendus*.

Patents in the Chemical Arts taken out in France.—The usual list for March last.

The Question of Coal-dust.—R. Galloway.—From *Nature*.

Properties and Proprietors of Ungreenable Aniline Black.—A continuation of the acrimonious discussion on ungreenable aniline blacks.

French Association for the Advancement of Sciences.—This Association has held its 15th session at Nancy under the presidency of M. Friedel. The meeting began on the twelfth and concluded on the 19th ult.

Industrial Society of Mulhouse: Session of the Chemical Committee.—June 9.—With reference to the prize proposed by M. Camille Kœchlin for an albumen steam orange not affected by steaming, M. Jacquet remarked that he had produced an orange of this kind six years ago by adding to the albumen chrome-orange, cad-

mium nitrate, and sodium acetate. M. Kœchlin replied that his proposed prize did not refer to means for preventing the sulphuration of chrome-oranges, but contemplated a new orange, free from lead.

Reale Accademia dei Lincei.

This contains a memoir by Augusto Righi on the cause of rotatory magnetic polarisation. He considers that the hypothesis by which Fresnel explains natural rotatory polarisation lacks experimental confirmation, since, in the case of quartz, the separation of the incident ray into two opposite circular rays obtained with the double or triple prism of Fresnel may be regarded as a special phenomenon of diffraction, whilst, in the case of bodies endowed with a rotatory magnetic power, the experiments of interference made to show a different velocity of propagation of the circular rays may be interpreted in another manner.

Journal de Pharmacie et de Chimie.

Vol. xiv., No. 4, August 15, 1886.

Decomposition of Hydrofluoric Acid by the Electric Current.—H. Moissan.—Already inserted.

Urethane from an Analytical Point of View.—Georges Jacquemin.—On treating a 1 per cent solution of urethane with a 5 per cent solution of mercuric chloride and then with potassa at 5 per cent there is formed an abundant white precipitate. This precipitate can be distinctly obtained in some c.c. of a solution containing 1.50 grms. of urethane in a litre of water. The author names this precipitate mercuric carbamate. Theoretically 0.1 of urethane dissolved in 10 c.c. of water and mixed with potassa in decided excess should be completely precipitated as a white mass by 10 c.c. of a standard solution of mercuric chloride at 1.522 per cent, and that, on adding a drop more, there should be produced a persistent yellow precipitate marking the completion of the operation. Experiment, however, showed that not 10 c.c. but 20 c.c. of the standard mercuric solution must be employed for the complete precipitation of 0.1 gm. of urethane. It is necessary to add a large excess of potassa to the urethane operated upon, and to stir with a rod after each addition of mercuric chloride. Very near the end of the operation there appears a very faint yellow tint, which must not be confounded with the yellow precipitate indicating the end of the operation.

Determination of Lime in Bone-Black.—P. Guyot.—In determining this lime it is common to boil a weighed quantity of the black with a solution of ammonium chloride and collect the free ammonia liberated, deducing from its quantity that of the quicklime. But as calcium carbonate in the states of chalk, limestone, &c., also decompose ammonium chloride, the volume of ammoniacal gas given off does not indicate the quicklime present.

On Chlorozone.—Drs. Lunge and Landolt.—The substance of this note has already appeared.

Essence of Boulogne is obtained by treating chloride of lime stirred up in water with sulphuric acid at 12° B., and receiving the gases in weak soda-lye.

Stannous Chloride as a Disinfectant.—Stannous chloride is considered equally effective with mercuric chloride, and has the advantage of being perfectly innocuous (?)

Centenary of the Death of Scheele.—This event was celebrated at the little town of Köping, in Sweden, on May 21, 1886.

Reagent for Sugar in Urine.—Into a test-tube, which should not be filled more than one third, are poured 5 to 6 c.c. of the urine to be tested; 1 c.c. of a solution of potassium ferrocyanide is added, then 1 to 1½ c.c. of potassa lye, and the whole is repeatedly boiled. If no sugar is present the liquid retains its yellow colour; if it contains sugar it becomes of deep brownish red.

Toxicity or Non-Toxicity of the Compounds of Copper.—After a long discussion the Belgian Academy of Medicine rejected the two following propositions which had been submitted by [Dr. Du Moulin, viz:—“Copper combined with articles of food in the proportions usually met with is not dangerous.” “Especially the greening of preserved vegetables with copper salts is absolutely inoffensive.” The Academy, on the contrary, adopted the following proposition, which will be transmitted to the Government:—“The compounds of copper are not merely useless in foods; they are injurious.”

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Griess's Test.—Can any of your readers tell me what chemical changes occur when meta-phenylene-diamine is acted upon by nitrous acid?—J. O. W. B.

OWENS COLLEGE, Victoria University, MANCHESTER.

CHEMISTRY COURSE.—Full particulars of this Course, qualifying for the Victoria University Degree in Chemistry and the College Technological Chemistry Certificate, will be forwarded on application. The SESSION commences October 5th.

HENRY WM. HOLDER, M.A., Registrar.

THE MASON COLLEGE, Birmingham. SESSION 1886-87.

FACULTIES OF ARTS AND SCIENCE.

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GEO. H. MORLEY, Secretary.

THE YORKSHIRE COLLEGE, LEEDS.

The 56th Session of the Department of Medicine begins on the 1st of October; and the 13th Session of the Department of Science, Technology, and Arts on October 4th.

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All communications should be addressed to Mr. A. NORMAN TATE, 9, Hackins Hey, Liverpool, as, owing to similarity of surname with that of the principal of another chemical establishment in Liverpool, misconception and mistakes have arisen.

THE CHEMICAL NEWS.

VOL. LIV. No. 1401.

ON SOME PROBABLE NEW ELEMENTS.*

By ALEXANDER PRINGLE.

THE subject of my paper is some of the results of chemical work upon the mineral constituents of my own landed property. That property is situated upon the River Tweed, in the county of Selkirk. It is mountainous. The rocks are believed by geologists to belong to the Lower Silurian formation, or, in other words, to be very old, and they have been uncommonly free from volcanic disturbance. The chief disturbances they have undergone have been caused by glaciers, weathering, and rain.

This subject is described as a paper "On some Probable New Elements." I had no expectation whatever of finding any new elements, but only a slight hope of getting some of the rarer ones in small quantity, such as might suffice to please a chemist if he found them upon his own estate.

I commenced my work upon the veins of crystalline quartz in the valleys, because these might be expected to contain within their interstices the filtrate from the rocks. Some of them were blocked up with ferric oxide and basic ferric salts. By working upon these I met with some mineral acids which were new and strange to me, and perplexing. But the labour of crushing the quartz was considerable, and the yield smaller than I can describe. I therefore tried to trace out the source from whence they came. It was evident they must have dissolved iron, and that the ferrous salts thus produced had travelled through the rocks in company with ferrous carbonate, and that the mixture, emerging into the open air, had precipitated basic ferric salts of unknown acids among other substances. Therefore I went up on to high ground, and followed the track of ferric precipitates. This track led me along the glacier lines to their extremity,—that is to say, to a high ridge over which the glaciers must have fallen, and here it ceased. Beneath the turf was gravel, which had evidently been deposited by the falling glaciers, for very many of the stones were shaped as they are in a "moraine profonde." A small waterfall had excavated fully 7 feet of this gravel, and when I stood in the drip of it, and could see within, I saw at the bottom what was like an asphalt pavement. This proved to be the main source of the iron, and gave a rich yield of the curiosities for which I had been searching.

I imagine it was the ancient soil of these very ancient mountains, and therefore represented, if I may so say, the cream of the rocks,—that glaciers had carried off nearly all of it into the Old Red Sandstone sea near Melrose, where its contents would be so distributed as to be difficult of recognition to chemists, but that at the spot where I found it the glaciers had covered it with their own *débris*, and thus protected it from their own action and from subsequent rains. When I got this glimpse of it Nature had recently formed the waterfall, but has since covered it up again, and the iron stains have disappeared that pointed out the way to it. I have found another similar deposit above the glacier lines.

The element which I am best prepared to describe is the one that has given me most trouble. I thought it judicious to tackle the chief difficulty first, because unless I could separate this element out I could not get the others in a state of purity. As I required to give it a name, even for my own convenience in making notes, I called it Polymnestum (Pm), because its compounds com-

bined with those of several other elements all at one time, and I had a difficulty in getting them away in combination with any one in particular, either as a precipitate or in solution.

This element is a metal of rather dark colour, but I have not yet succeeded in fusing it so satisfactorily as to venture upon its description. Its equivalent is about 74, but before speaking definitely on this point I wish to try more experiments, as my results hitherto have varied by a few decimals.

There are four oxides. In the first of these one equivalent of the metal is combined with one of oxygen, in the second with two, and in the third with three. As to the fourth I have some doubt as yet, but will describe it in its place as far as I can.

The monoxide is bright green, and its hydrate white. Its salts are some of them green and some white. It is soluble in solutions of all the alkalies and alkaline carbonates. With the fixed alkalies these solutions are green. The monosulphide is not precipitated from them till after the lapse of a long time. Then it falls like ferrous sulphide, of a dark green colour. When dried, even in sulphuretted hydrogen, this becomes nearly white, but regains the dark colour when moistened. It dissolves in weak acids, such as the acetic. The sulphate of the monoxide, which is white, is insoluble in water, in excess of sulphuric acid, and in all other acids. It dissolves, however, in concentrated sulphuric acid, and is re-precipitated upon dilution. It also dissolves when boiled with carbonate of soda, and is of course re-precipitated by any acid. The metal, therefore, can be very well separated out as sulphate of the monoxide. The oxalate forms with the alkalies double oxalates, which are sparingly soluble. Salts of the monoxide give white precipitates with iodide of potassium, and with borates and phosphates. If tartaric acid be added to them, and then an alkali, the tartrate precipitates without boiling. It is white and crystalline, but if long exposed to the air effloresces and becomes green. If it is heated with nitrate of ammonia the mass swells up, producing the dioxide. It then takes fire and leaves the trioxide. The monochloride when once dried is not readily dissolved by water. It is white, and gives no reaction with ferrocyanide or ferricyanide of potassium. If the dichloride is heated in hydrogen it is reduced only to this monochloride, and as such volatilises at a very moderate heat. Solutions of the salts corresponding to the monoxide are very liable to pass into those corresponding to the dioxide through lapse of time, but they can be reduced to their former condition by treatment with tartaric acid.

The dioxide resembles in appearance ferric oxide. Most of its salts are soluble and yellow. I am acquainted with an insoluble basic sulphate which is yellow, and basic acetate which is fawn-coloured. But the best precipitant I know of is sulphide of ammonium. The disulphide is dark brown, insoluble in acetic acid, but soluble in hydrochloric acid when freshly precipitated. The dichloride is white when dry, but yellow in solution and deliquescent. It is not soluble in alcohol or ether. It gives with ferrocyanide of potassium a white precipitate, and with ferricyanide a yellow one. The salts of the dioxide form double salts with those of ammonia which are not precipitated by ammonia, but fixed alkalies precipitate the dioxide.

The trioxide is white. It is not fused or volatilised at a white heat. It dissolves very slightly in pure water, a little more in hydrochloric, nitric, or dilute sulphuric acid, and more still in hot concentrated sulphuric acid. If its solution in water or a dilute acid is treated with sulphuretted hydrogen a pale yellow sulphide falls, which dissolves in alkaline sulphides, and is easily oxidised by heating with nitric acid. It appears to be a sesquisulphide. The trioxide acts the part of an acid. It is not easily made to combine even with caustic potash in the wet way, though it does so readily when the alkali is fused. It forms double salts with the alkalies and many

* Read before the British Association, Birmingham Meeting, Section B.

metallic oxides. Most of its salts are soluble; they are not decomposed by sulphuric or any other acid at any temperature; they give precipitates in presence of strong acids with salts of baryta, strontia, mercurous oxide, and lead oxide, and in presence of acetic acid with salts of lime. The barium precipitate is the most complete under all circumstances; it is not at all decomposed by boiling with alkaline carbonates for two hours, but it is so by fusion with them. In short, the salts of the trioxide greatly resemble sulphates, but they are even more stable, and form double under a great many circumstances. If the trioxide is heated with chlorate of potash or nitrate of ammonia it is further oxidised, becoming pink.

I am unwilling to believe, without the evidence of repeated experiments, that a pentoxide is here produced, but the following experiment appears to prove that it is so:—I heated 100 grains of the sulphate of the monoxide with nitrate of ammonia till the weight was constant, and it was then 89.6 grains. This corresponds to five equivalents of oxygen and one of the metal taken as 74.01. Scarcely any remnant of sulphur could be detected by fusing with sodium and testing with nitro-prusside of sodium. Nessler's test showed no ammonia to be remaining, and sulphate of brucine no nitric acid.

The qualitative test which I use for detecting this metal is as follows:—I see that if the metal is present it must be as a salt of the trioxide. This can be done by fusing a mineral with caustic alkali and dissolving with hydrochloric acid, or by dissolving with hydrochloric and heating for some time with nitric acid. I then precipitate from the strongly acid solution with chloride of barium, and heat the precipitate with about half its bulk of sodium. This is sure to show some of the green monoxide, which is very characteristic. I then usually test with nitro-prusside of sodium to see whether any part of the barium precipitate was sulphate. The advantage of using sodium, which should be in one lump, is that it does not reduce the whole precipitate equally. In whatever proportion the trioxide may be present, that which is next the sodium will be reduced to metal, and what is farther off to monoxide. An additional test is to reduce all to metal which ought to be insoluble in hydrofluoric, hydrochloric, and nitro-hydrochloric acids; but if part of the precipitate was sulphate, some of the monosulphide will be formed which dissolves in acids. A third test is to heat the precipitate with chlorate of potash, and see whether the product is pink.

I have indicated that I believe there are other new elements in the mineral in question, but I shall only mention these now in the briefest possible manner.

One of them greatly resembles iron, and is slightly attracted by the magnet; it forms a monoxide, sesquioxide, and trioxide. The trioxide is exceedingly like the trioxide of the metal last described. But the most remarkable circumstance is that the sesquichloride yields a kind of prussian-blue. With sulphocyanides it gives no colouration and with tinctures of galls a light brown precipitate, and it can be easily distinguished from ferric chloride in other ways. The double salts, however, which it forms with the alkaline chlorides are very like the ferric ones. This prussian-blue is more beautiful, but less insoluble than ferric ferrocyanide.

Another metal, of which the equivalent is 95.4, is as black as charcoal, and its lowest oxide is almost equally dark coloured when dry and dense, though otherwise brown. I therefore call it Erebodyum (Eb). I am best acquainted with the dioxide, which resembles oxide of bismuth in its tendency to produce insoluble basic salts, although not precisely in the same way, and there are no oxy-salts that I know of. There appears to be also a higher oxide, of a pink colour, like the highest one of Polymnestum, and obtained in the same way. The oxalates of this and the preceding metal are scarcely at all soluble in oxalic acid.

There is a metal which I call Gadenium (a local name). I usually find its equivalent to be 43.6, but I have also

made it as low as 43.547. I have not yet tried to fuse it, but the powder is light grey. The monoxide is red, yielding white salts, and the dioxide cream-coloured, yielding yellow salts. One of the unusual precipitates it gives is the sulphocyanide.

Another metal, of which I cannot yet mention the equivalent with any certainty, resembles lead in colour and softness, and is easily fused and volatilised. It gives yellow and green salts, and in some respects is like nickel and cobalt.

Lastly, there is a non-metallic or semi-metallic element of which the equivalent is 45.2. I think it the most interesting of the group, and could describe it at considerable length. Its colour is red, and when it has a metallic lustre it looks so like a sunset sky that I have thought of calling it Hesperine, or perhaps Hesperisium (He). It has a monoxide, sesquioxide, and dioxide. The last two form acids which precipitate barium from acid solutions. In fact this element resembles selenium very much. It forms gaseous compounds with hydrogen and with fluorine, and combines with all the other elements at one temperature or another, except perhaps with nitrogen.

ON THE ARSENATE OF CALCIUM AND AMMONIUM

By CHARLES L. BLOXAM.

IN a recent communication to the CHEMICAL NEWS (vol. liv., p. 16) I recommended the addition of arsenic acid to a solution of calcium sulphate mixed with ammonia, for the detection of calcium in the presence of strontium. I then believed that the beautiful crystalline precipitate was the ammonio-calcic arsenate described by Wach (quoted in Gmelin's "Handbook," Watts's edition, vol. iv., p. 306) as containing, in 100 parts,—

NH ₃ .	2CaO.	AsO ₅ .	14HO.
5.35	17.52	35.83	41.15.

If this formula be written NH₄O.2CaO.AsO₅.13HO, the percentage of water (HO) becomes 38.32, whilst that required by the formula is only 37.26. The formula NH₄O.2CaO.AsO₅.14HO requires 39 per cent, which agrees better with that found by Wach (38.32).

Gmelin remarks that "the resemblance of this compound to the phosphate of magnesia and ammonia leads to the supposition that the quantity of water which it contains does not exceed 13 atoms"—

(NH₃.2CaO.AsO₅.13HO, or NH₄O.2CaO.AsO₅.12HO).

With regard to the phosphate referred to, the formula NH₄O.2MgO.PO₅.12HO requires 44 per cent water. Wach found 45.06 per cent, and Otto found 45.15.

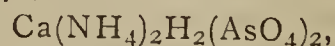
The formula NH₄O.2MgO.PO₅.13HO requires 46.06 per cent water.

Analysis, therefore, gives rather more water than 12HO in the phosphate, and rather less than 14HO in the arsenate. In modern notation the former appears to be NH₄.MgPO₄.6H₂O, and the latter NH₄.CaAsO₄.7H₂O.

In "Watts's Dictionary" (i., 381) the salt—



which, with Ca=40, would become—



is described as having been obtained by Baumann, by adding ammonia in excess to a solution of dicalcic arsenate in nitric acid, as a flocculent precipitate soon changing to a mass of needle-shaped crystals. This behaviour corresponds exactly with that of the precipitate formed by adding arsenic acid to a solution of calcium chloride mixed with excess of ammonia, and the sudden transformation of the opaque amorphous precipitate into the transparent shining needles can be recommended as a class experiment. The precipitate is almost absolutely

insoluble in weak ammonia, though it dissolves slightly in water. Thinking it remarkable that an acid arsenate represented by Baumann's formula should be formed in a solution containing a large excess of ammonia, I proceeded to repeat the analysis.

(1.) A weighed quantity of Iceland spar was dissolved in HCl, the solution boiled to expel CO₂, mixed with NH₃ in large excess, and arsenic acid added until no further precipitation took place; the liquid was briskly stirred, set aside for a few minutes, the precipitate collected on an air-dried weighed filter, thoroughly washed with weak ammonia (sp. gr. 0.958), and exposed freely to the air, in July, until it had ceased to lose weight after an interval of eighteen hours. This required six days and nights.

10.06 grains CaCO₃ gave 32.15 grains of the air-dried precipitate.

CaNH₄AsO₄·7H₂O requires 32.49 grains.
CaNH₄AsO₄·6H₂O „ 30.68 „
Baumann's formula „ 35.81 „

Finding that the loss of weight was very small towards the end, and that the rate was uniform, the precipitate was weighed, in the following experiments, as soon as the loss of weight in eighteen hours had fallen to 0.1 grain.

(2.) 5.5 grains CaCO₃ gave 16.68 precipitate, or 323.9 per cent.

(3.) 6.15 grains CaCO₃ gave 19.92 precipitate, or 323.9 per cent.

CaNH₄AsO₄·7H₂O requires 323 per cent.
CaNH₄AsO₄·6H₂O „ 305 „

As there was no calcium found in the filtrate, all that present in the CaCO₃ employed existed in the precipitate, and would amount in (2) and (3) to 12.35 per cent. The formula requires 12.38 per cent.

(4.) 8.35 grains of the air-dried salt were dissolved in HCl, ammonium acetate added, the Ca precipitated with ammonium oxalate, and the filtrate precipitated by a mixture of MgSO₄, NH₄Cl, and NH₃. The—

MgNH₄AsO₄·½aq,

dried at 100°, corresponded to 22.78 per cent of arsenic.

CaNH₄AsO₄·7H₂O requires 23.22 per cent.

(5.) 7.765 grains of the air-dried arsenate were boiled with an excess of silver nitrate, which effected complete decomposition. The silver arsenate (Ag₃AsO₄) weighed 11 grains, corresponding to 1.7818 of arsenic, or 22.94 per cent. The filtrate had a very feebly acid reaction, and did not retain any silver arsenate in solution, showing that no nitric acid had been liberated, and that the arsenate was normal and not acid in constitution.

(6.) 8.05 grains of the air-dried salt were boiled with excess of potash, the NH₃ absorbed by standard sulphuric acid, the excess of which was determined by standard lime-water. The NH₃ amounted to 0.4253, or 5.28 per cent.

CaNH₄AsO₄·7H₂O requires 5.57 per cent.

(7.) 31.44 grains of the air-dried salt were exposed in the air-pump vacuum over sulphuric acid till there was no further diminution in weight of any importance. This required a fortnight's exposure. The loss amounted to 36.6 per cent of the weight of the air-dried salt.

(8.) 32.15 of another sample lost 37.41 per cent.

(9.) 8.2 grains of the vacuum-dried salt, boiled with potash, gave 2.96 per cent of NH₃.

(10.) 6.39 grains gave 2.89 per cent of NH₃.

(11.) 4.65 grains of the vacuum-dried salt were heated over an Argand burner in a small flask through which air was slowly aspirated. The loss amounted to 0.76, or 15.41 per cent.

(12.) 10.53 grains, in a similar experiment, lost 1.64 grains, or 15.57 per cent.

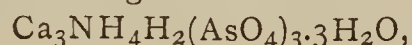
(13.) 5.52 grains thus heated, the ammonia being condensed in standard sulphuric acid, lost 0.86, or 15.58 per cent, and gave 0.1437 NH₃=2.6 per cent, leaving for the water 12.98 per cent.

(14.) 49.32 grains Iceland spar entirely converted, as in (1), into the ammonio-arsenate, and dried *in vacuo* over sulphuric acid, without previous air-drying, gave 100.3 grains of the salt, which therefore contained 19.67 per cent of calcium.

(15) 6.03 grains of the vacuum-dried salt, boiled with excess of silver nitrate and filtered, gave a strongly acid filtrate, which was found, by neutralising with standard solution of sodium carbonate, to contain 1.2256 grains of HNO₃, or 20.82 for 100 of the salt taken.

(16.) 5.96 grains of the vacuum-dried salt, treated as in (15), left undissolved 11.42 grains of Ag₃AsO₄, of which an additional 1.9 grains were precipitated on neutralising the filtrate with sodium carbonate. This corresponds to 36.2 per cent of arsenic.

These numbers represent the salt dried *in vacuo* over sulphuric acid as having the formula—



which requires in 100 parts—

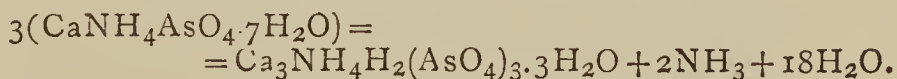
	Ca.	As.	NH ₃ .	Loss (NH ₃ and H ₂ O) on ignition.
	19.46	36.82	2.78	16.03
Found	19.67	36.20	2.89	15.58
„	20.00	—	2.96	15.57
	—	—	—	15.41

The action of silver nitrate upon the salt would be expressed by the equation—



This would require two molecules, or 126 parts by weight, of HNO₃ to be liberated on decomposing one molecule, or 611 parts by weight of the salt by silver nitrate; or 20.62 of HNO₃ should be liberated by 100 of the salt. In (15) the amount liberated was shown to be 20.82.

The change in composition of the air-dried salt by being exposed, at the common temperature, *in vacuo*, over sulphuric acid, is expressed by the equation—



This would require the air-dried salt to lose 36.94 per cent *in vacuo*. In (7) it lost 36.6, and in (8) 37.41 per cent.

(17.) In order to ascertain the formula of the salt dried at 100°, 7.33 grains of Iceland spar were treated as before, and the precipitate dried in the water-oven till of constant weight. It weighed 14.66 grains, and therefore contained 20 per cent of calcium.

(18.) 10.49 grains CaCO₃ gave 21.35 grains of the salt dried at 100°; corresponding to 19.66 per cent of calcium. Hence the salt dried at 100° contains the same proportion of calcium as the vacuum-dried salt.

(19.) 7.52 grains of the salt which had been dried at 100°, when boiled with silver nitrate, gave a total quantity (16) of 18.1 grains Ag₃AsO₄; corresponding to 39 per cent of arsenic. The nitric acid liberated was 2.0228 grains.

(20.) 8.2 grains of the salt dried at 100°, when boiled with potash, gave 0.1191 grain of NH₃, or 1.45 per cent.

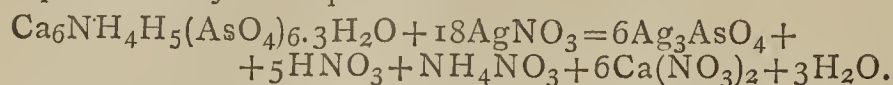
(21.) 8.995 grains gave 0.1471 grain of NH₃, or 1.64 per cent.

(22.) 11.62 grains of the salt dried at 100°, heated as in (11), evolved 1.0976 of water, or 9.45 per cent, and 0.0524 grain of NH₃. On boiling the residue with potash it evolved 0.1242 grain more NH₃, making in all 1.52 per cent of NH₃.

These results give, for the salt dried in the water-oven, the formula Ca₆NH₄H₅(AsO₄)₆·3H₂O, which requires, in 100 parts,—

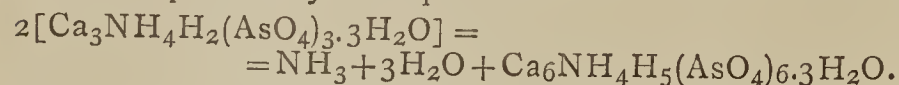
	Ca.	As.	NH ₃ .	H ₂ O.
	20.85	39.10	1.48	9.38
Found	20.00	39.00	1.45	9.45
„	19.66	—	1.64	—
	—	—	1.52	—

The action of silver nitrate upon this salt would be represented by the equation—



This would require five molecules, or 315 parts by weight of HNO_3 to be liberated by one molecule, or 1151 parts of the salt; or 27.37 of HNO_3 for 100 of the salt. In (19) the quantity liberated was 26.90 per cent.

The change in the vacuum-dried salt, when heated to 100° , is expressed by the equation—



This would require the vacuum-dried salt to lose 5.81 per cent at 100° .

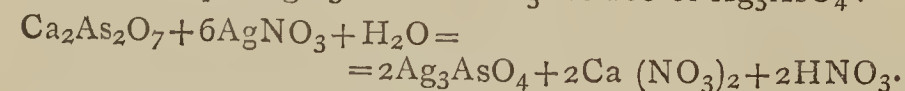
By experiment the loss amounted to 5.77 per cent.

When the salt dried at 100° was ignited it became slightly brown, and the residue was feebly alkaline. When analysed it gave—

	I.	II.	III.	IV.
Ca ..	25.8	25.00	25.74	25.58 per cent,
As ..	43.0	41.01	—	—

the different samples varying a little in composition, as more arsenic was lost at higher temperatures, but agreeing fairly well with the formula $\text{Ca}_2\text{As}_2\text{O}_7$, which requires 23.1 per cent of calcium and 43.86 per cent of arsenic.

When boiled with silver nitrate it was not completely decomposed, but 13.73 of HNO_3 were liberated for 100 of Ag_3AsO_4 produced, which would justify the following equation, requiring 13.61 of HNO_3 for 100 of Ag_3AsO_4 :—



A little As_2O_3 and AsH_3 are evolved during the strong ignition of the salt.

It appears, therefore, that the precipitate produced by arsenic acid in a solution of calcium chloride containing free ammonia has the composition—

Air-dried	$\text{CaNH}_4\text{AsO}_4 \cdot 7\text{H}_2\text{O}$
Dried in <i>vacuo</i> over sulphuric acid ..	$\text{Ca}_3\text{NH}_4\text{H}_2(\text{AsO}_4)_3 \cdot 3\text{H}_2\text{O}$
Dried at 100°	$\text{Ca}_6\text{NH}_4\text{H}_5(\text{AsO}_4)_6 \cdot 3\text{H}_2\text{O}$
Ignited	$\text{Ca}_2\text{As}_2\text{O}_7$.

In view of the trivalent function of the arsenate radical, AsO_4 , these changes in the composition of the calcium-ammonium salt are the simplest which could occur.

Determination of Calcium as Ammonio-Arsenate.

The determination of calcium in this form has many advantages over the precipitation as oxalate. Being so highly crystalline the precipitate filters much more rapidly, and is not liable to run through the filter, as is often the case with the oxalate unless it is boiled in the liquid. The filtration and washing of the ammonio-arsenate are effected continuously, so that the operator may conclude them at once without turning to another subject. The calcium constitutes about one-fifth of the weight of the precipitate dried at 100° , whereas it forms about two-sevenths of calcium oxalate dried at 100° , so that errors tell more upon the calcium in the case of the latter. This source of error is of course still more important when the oxalate is converted into carbonate or oxide for weighing, and even as sulphate the weight is only about three times that of the calcium to be determined.

The disadvantages of the arsenate are that it must be washed with ammonia-water, and collected on a weighed filter, and that it must be dried for some hours in the water-oven. If it be ignited it suffers an uncertain loss of arsenic.

It has been pointed out above that the salt dried at 100° has a formula which requires 20.85 per cent of calcium, but if it be weighed after ordinary drying in the water-oven, the temperature of which is never quite 100° , it is safer to take it as containing 20 per cent of calcium,

as the following experiments prove. They were made as in (1), the precipitates being collected on filters previously dried in the water-oven and weighed.

	I.	II.	III.	IV.
Ca taken (as Iceland spar)	2.932	4.116	4.024	3.936
Ca calculated as 20.85 per cent of precipitate.. ..	3.057	4.451	4.043	4.034
Ca calculated as 20 per cent	2.932	4.270	3.878	3.870

As a mean of these results, for 3.752 grains of calcium taken, 3.896 grains were found if the precipitate was calculated as containing 20.85 per cent of calcium, and 3.737 if 20 per cent was allowed, giving an excess of 3.83 per cent on the calcium in the former case, and a deficiency of 0.4 per cent in the latter.

The determination of the calcium as oxalate is susceptible of much greater accuracy than this in very careful hands, but the much greater volume of the arsenate renders it far easier to avoid loss.

The ammonia used for washing is that commonly used in the reagents, containing about 8.5 per cent by weight of NH_3 , and I find it convenient to keep a rubber stopper fitted with washing-bottle tubes, which may be inserted in place of the stopper of the ammonia bottle. The precipitate is liable to crystallise on the sides of the beaker, especially if they be touched by the stirring-rod, but is easily detached.

The ammonio-arsenate method is very suitable for determining calcium in river and spring waters, on account of its volume being so much greater than that of the oxalate. Should the analyst prefer to convert it into oxalate instead of drying, it may be dissolved off the filter with acetic acid, and the solution mixed with ammonium oxalate. The magnesium contained in the water is also precipitated as ammonio-arsenate, and may be re-precipitated from the acetic solution filtered from the calcium oxalate, by adding excess of ammonia; the precipitate of magnesium ammonio-arsenate is collected on a dried weighed filter, washed with ammonia, dried at 100° , and weighed as $\text{MgNH}_4\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. I have found it much quicker to determine the Ca in waters in this way than by the old process. A much smaller quantity of water is necessary, and if the calcium be eventually required in the form of oxalate the bulk of liquid in which it is precipitated is not more than one-tenth of the original volume of water.

A very easy determination of the joint amount of Ca and Mg for checking the soap-test may be made by mixing 100 c.c. (or even less) of the water with excess of ammonia, and adding arsenic acid. After briskly stirring for a minute or two, and standing for ten minutes, the precipitate is collected on a dried weighed filter, and dried at 100° till constant. Half the weight of the precipitate may be taken as the weight of CaCO_3 (or its equivalent in hardness) present in the water. Since 100 of MgCO_3 correspond to 226 of the magnesian precipitate (instead of 200 as for calcium) the result is less accurate, as the proportion of Mg in the water is greater.

In applying this method to the water of the laboratory (Grand Junction) three determinations were made, 100 c.c. of water being taken for each: the ammonio-arsenate weighed 0.66, 0.67, and 0.68 grain, corresponding to a mean of 0.335 of CaCO_3 , or 15.22 grains per gallon, a result almost identical with the hardness determined by the soap-test.

The last two precipitates were dissolved off the filters by acetic acid, the calcium precipitated by ammonium oxalate, and the precipitates, after boiling, collected upon the same filters, and dried at 100° .

The weights of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ obtained were 0.45 and 0.44 grain, corresponding to a mean of 0.3048 of CaCO_3 , or 13.85 grains per gallon. On adding excess of ammonia to the filtrate a small precipitate of magnesium ammonio-arsenate was obtained, which could not be weighed. The determinations were easily completed in two hours.

King's College, London, September 1, 1886.

ON THE
PURPLE OF THE SOLAR SPECTRUM.

By M. CAMILLE KÖEHLIN.

IN the solar spectrum there are found only two simple colours, blue and yellow. The third is blended with the yellow and the blue to form on the one side the reds and on the other the violets. The purple is the red minus the yellow or the violet minus the blue, or again, the spectrum without yellow or without blue. If we project upon the red of one spectrum the blue of a second spectrum, or the yellow of the latter upon the violet of the first, we obtain purple. We can restore the red or the violet by projecting respectively upon the purple the yellow or the blue of a third spectrum. If these superpositions are effected with reversed prisms so that the complementary colours reciprocally cover each other, the spectrum presents at each extremity a purple region with a yellowish-white interval.

If we gradually suppress the light of a spectrum at the purpled extremity the fading colours leave purple for a last trace.

Although the red tones of the spectrum become poorer in yellow, the further they remove from that colour they reach their extreme limit without displaying the purple in its characteristic purity. The yellow on one hand and the blue on the other share between themselves the purple of the prismatic spectrum, even to the last traces. It would not be the same in spectra without interruption of continuity, such as are shown by nacreous irisations, by soap-bubbles, crystals, supernumary rainbows, and the twilight illuminations of the clouds. If we establish a bare interval in a green ground we have the impression of purple, which is the colour complementary to green. Compound colours correspond to the simple colours, and inversely.

The purple colouration is very rare among mineral compounds. We shall mention only the ruby, the enamels of gold and of copper, and certain flames. In the vegetable kingdom purple is next in abundance to white and yellow. The roses, pinks, cinerarias, fuchsias, geraniums, present types of it in all intensities. Rose is dilute purple, not dilute red, which would give flesh-colours. Among dye-drugs we have magenta (salts of rosaniline), the red-woods, ammoniacal cochineal, the methylic eosines, xylidine red, pseudopurpurine, alizaramide, and, by right of antiquity, murexide or Tyrian purple. A curious fact in this assortment of colouring-matters is that none of them gives a fast purple. This problem would be of the greatest importance not merely in virtue of a beauty of shade surpassing all others, but because it would give the means of compounding by mixtures, reds more or less inclining to carmine, amaranths, and fast pines, which cannot be obtained with reds containing yellow. In place of pines it would be the industrial violet (of madder) which does not exist in the spectrum, because it represents a mixture of red and blue and not of purple and blue.

Purple being a simple colour will never be obtained by mixtures, any more than we can obtain a yellow by mixtures. We can arrive at purple only by eliminating the yellow from a red or the blue from a pine.

Red, properly speaking (the conventional scarlet) is more common among mineral products than is purple. It is the colour of vermillion, of mercuric iodide, of cochineal scarlets, coralline, xylidine, eosine, and of certain alizarine reds. If, in the vegetable kingdom, red flowers are not as common as purple flowers, there is one which may be considered as the type of reds, the field poppy (*Papaver Rhæas*). We may thus distinguish neutral reds from reds in which either purple or yellow predominates, such as cherry, fire, nacarat, orange, capucine, &c.

The solar spectrum contains the elements of all colouration, either by mixtures, by dilutions with white, or by extinction with black. In the latter case the colours containing blue retain their tint, whilst those on the yellow

side are changed. Thus green, blue, and violet give what are called heavy greens, heavy blues, heavy violets, whilst yellow, orange, red, and purple cannot be deepened, but become olive, brown, garnet, or amaranth.—*Comptes Rendus*, ciii., p. 432.

VERIFICATION OF THE CALCULATION OF
THE ATOMIC WEIGHTS OF M. STAS.*

By J. D. VAN DER PLAATS.

(Continued from p. 164.)

XXI. *Synthesis of Nitrate of Lead*, a 303.

THE atomic weight of lead formed the subject of several researches of Berzelius. This illustrious man, "whose analytical exactitude has never been surpassed, if even ever equalled, no matter by whom" (Stas, a 208) found, while reducing oxide of lead by hydrogen, values varying from 207.16 to 207.02, the mean being 207.1. M. Stas has sacrificed an enormous amount of time to preparing pure lead, but it always contained 5-100,000ths of potassium and sodium, with traces of copper and iron. These impurities, forming alkaline nitrates, augment the weight of the nitrate of lead by about 0.007 grms. per 100 grms. of lead. Further, there exist doubts as to the degree of desiccation of the salt, which is decomposed at 195°, and does not lose all its water even at 140°.

M. Stas has made two series of syntheses; in the first the nitrate was dried in a current of air; in the second the drying operation was conducted *in vacuo*. I have availed myself of the results of the latter series.

Lead.	Nitrate of Lead.	Pb : PbN ₂ O ₆ = 100.
103.000	164.773	159.9738
140.6887	225.0674	159.9755
110.2672	176.408	159.9860 *M
141.9927	227.1527	159.9749
148.616	237.702 (?)	159.9438 * (?)
124.348	198.924	159.9736

Mean of the first series 159.9713*

100.000	159.970	159.970
200.000	319.928	159.964
250.000	399.8975	159.959 <i>m</i>
250.000	399.914	159.9656

Mean of the second series 159.9646

Log = 2.2040239

Mean of the ten estimations 159.9686

Log. = 2.2040347

XXII. *Synthesis of Sulphate of Lead*, a 308.

The impurities of the lead diminish the relation, whilst the air condensed on the sulphate might possibly augment it. M. Stas declares "that there is no estimation which offers so many difficulties and uncertainties."

Lead.	Sulphate of Lead.	Pb : PbSO ₄ = 100.
141.9925	207.9388	146.4435 M
148.616*	217.6141	146.4270
100.000	146.419	146.419 <i>m</i>
200.000	292.864	146.432
250.000	366.0525	146.421
250.000	366.0575	146.423

Mean 146.4276

Log. = 2.1656230

It was the nitrates of experiments 4, 5, 7, 8, 9, and 10 that were turned into sulphates.

* *Ann. Chim. Phys.*, 6th Series, vol. vii., April, 1886.

We shall deduce from these twenty-two proportional relations the atomic weights of ten simple bodies.

We will take as the basis, oxygen, $O = 16$.

A. Atomic Weight of Silver.

If we take the relations I. and II.—

$$\begin{aligned} \text{Ag}_2 : \text{Ag}_2\text{S} &= 1 : a \\ \text{and } \text{Ag}_2\text{SO}_4 : \text{Ag}_2 &= 1 : b, \text{ then} \\ \text{Ag} &= \frac{32}{\frac{1}{b} - a} \text{ and } \text{S} = \frac{a-1}{\frac{1}{b} - a} 64 \end{aligned}$$

These two values are *independent* of all other atomic weights.

Again, let us take the relations III. and IV.—

$$\begin{aligned} \text{Ag} : \text{AgCl} &= 1 : c \\ \text{and } \text{AgClO}_3 : \text{AgCl} &= 1 : d, \text{ then} \\ \text{Ag} &= \frac{d}{1-d} \cdot \frac{48}{c} \text{ and } \text{Cl} = \frac{d}{1-d} \times \frac{c-1}{c} 48 \end{aligned}$$

In the same manner we can calculate the relations V. and VI., VII. and VIII. A fifth value for silver is deduced from IX. and X.

If $\text{KClO}_3 : \text{KCl} = 1 : e$, and

$\text{Ag} : \text{KCl} = 1 : f$, then we have

$$\text{Ag} = \frac{e}{1-e} \cdot \frac{48}{f}$$

We can obtain the lowest values for the atomic weight of silver by combining the minima of the relations of a and b , the maximum of c , and the minimum of d , &c. The maxima of a and b , the minimum of c , and the maximum of d give the highest values. By combining the averages we deduce the most probable figure.

In the following table I give the extreme and the average values. The variation between the extremes gives a better idea of the exactitude of the mean than the calculation of least squares. The numbers in parenthesis have been calculated with the mean of the relations of III., IX., and XXI., which is less probable for the reasons stated above. (See Table A).

If we call *uncertainty* that quantity by which the true value *might* differ from that which we accept as correct, whilst a value more removed might be considered as very improbable, I think we must admit the following:—

Degree of uncertainty.

$$\text{Ag} = 107.930 \dots \dots \dots 0.01$$

which signifies that, according to the present state of science, the atomic weight of silver cannot be higher than 107.94 nor lower than 107.92, whilst the most probable value is 107.93.

B. Atomic Weights of Chlorine, Bromine, Iodine, and Sulphur.

We have already indicated the method adopted for calculating an independent value of the atomic weight of each of these simple bodies. We obtain two new values by admitting that $\text{Ag} = 107.93$. (See Table B).

Which leads me to admit the following:—

Uncertainty.

$$\begin{aligned} \text{Cl} &= 35.456 \dots \dots \dots 0.005 \\ \text{Br} &= 79.955 \dots \dots \dots 0.01 \\ \text{I} &= 126.857 \dots \dots \dots 0.01 \\ \text{S} &= 32.06 \dots \dots \dots 0.01 \end{aligned}$$

(To be continued).

TABLE A.

Silver.

Atomic Weight.			Maximum.	Minimum.	Mean.
From the Relations of the Tables.		From the Syntheses and Analyses of			
I. II.		Ag_2S and Ag_2SO_4	107.9771	107.8690	107.9269*
III. IV.		AgCl and AgClO_3	107.9492	107.9271	{ 107.9345*
V. VI.		AgBr and AgBrO_3	107.9440	107.9002	{ [107.9387]
VII. VIII.		AgI and AgIO_3	107.9539	107.9112	{ 107.9221
IX. X.		KClO_3 and $\text{Ag} : \text{KCl}$	107.9520	107.8820	{ 107.9313*
					{ 107.9330
					{ [107.9150]

Mean of the five independent figures 107.9296

TABLE B.

Chlorine.

III. IV.	Independent value.	35.4537	35.4519	{ 35.45645*
				{ [35.45225]
III.	AgCl	35.4547	35.4456	{ 35.4550
IV.	AgClO_3	35.4711	35.4508	{ [35.4494]
				{ 35.46095

Bromine.

V. VI.	Independent value.	79.9629	79.9366	79.9497*
V.	AgBr	79.9586	79.9526	79.9556
VI.	AgBrO_3	79.9769	79.9068	79.9418

Iodine.

VII. VIII.	Independent value.	126.8759	126.8423	126.8572
VII.	AgI	126.8645	126.8470	126.8557
VIII.	AgIO_3	126.8990	126.8235	126.8585

Sulphur.

I. II.	Independent value.	32.0781	32.0347	32.0588*
I.	Ag_2S	32.0641	32.0528	32.0597
II.	Ag_2SO_4	32.0891	32.0362	32.0616

ANALYSIS OF SILICATES IN CONNECTION WITH BLOWPIPE DETERMINATIONS.

By W. M. HUTCHINGS.

ALL mineralogists who are accustomed to make use of the blowpipe for analysis are painfully aware that, as regards the largest of all the classes of minerals, the silicates, that very valuable instrument and its accessories can only suffice for a more or less satisfactory preliminary examination, and that for a complete qualitative knowledge of the composition of the specimens the "wet way" has to be called in. This is always comparatively tedious and troublesome, and specially so in the case of minerals which are not capable of being directly decomposed by hydrochloric acid. It is, of course, a very neat and comparatively speedy operation to fuse the mineral with sodium carbonate in a charcoal mortar, after wrapping the mixture in "soda-paper," as directed in Plattner's book; and the following wet analysis does not take a long time, but it seemed to me that it could be still further improved, both as to the time required and as to the number of "wet" operations involved. This is of importance, because the object of all chemists who practise blowpipe-work should be to get as far as they possibly can with "dry" operations, and so reduce as much as possible the quantity of chemicals in liquid form which must find a place in the portable laboratory.

Having recently had occasion to rapidly examine several silicates, I have tried another method, which has proved so satisfactory that I think it worth while to recommend it to others.

I decompose the silicate by means of ammonium fluoride, and fuse the fluoride residue with sodium carbonate, thus removing the silica and separating the bases into two groups rapidly, and entirely with "dry" reagents.

For the purpose in view, namely, mineral determinations, our attention is only required to be given to a very few constituents. Alkali we determine by flame-colouration. Also, before taking to the wet way, our blowpipe tests have shown us what metallic oxides are present. All we need consider in our wet analysis will be the alkaline earths and alumina, approximately their relative amounts, and that of the oxides of iron to alumina in some cases.

The fusion of the fluoride residue with sodium carbonate and solution of the fused mass in water gives us alumina in solution, leaving alkaline earths and oxide of iron undissolved. The separation, properly carried out, is very perfect, whether we have relatively much or little alumina to deal with. After filtration the solution is of course acidified, boiled, and alumina precipitated by ammonia. The insoluble portion in the filter is washed, and dissolved in a few drops of acid into a test-tube. If barium or strontium are suspected in the mineral, a drop of H_2SO_4 will prove their presence and remove them. The iron is then precipitated by ammonia, and tests applied for Ca and Mg as usual.

We by this method avoid the tedious solution of the mineral (after fusion with soda) in HCl, and the troublesome evaporation to dryness and removal of the SiO_2 . We also escape that most unpleasant operation, separation of Al_2O_3 and Fe_2O_3 by caustic alkali. I think anybody who makes trial of this plan will speedily see a great gain in time and convenience, as well as neatness.

About 50 to 75 m.grms. of very finely powdered mineral should be taken. I use a little bone spoon which when full holds about 150 m.grms. of an average silicate, and I take this half full of mineral powder, which is placed in the bottom of the small platinum spoon. The mineral is then covered with three heaped-up bone spoons of ammonium fluoride (say seven to eight times the weight of the mineral), which just fills the platinum spoon. This is then held over a small spirit-flame. The ammonium fluoride at once melts in its water of crystallisation, and

the mineral should be stirred up with a platinum wire. It is rapidly attacked, and a syrup is formed in the spoon, which is then evaporated down. Very little loss takes place from spirting of the mass. When dryness is nearly reached care must be taken, and the last portion of the operation carried on at low heat (barely incipient redness at the finish), as in some cases, where much alkali is present, the fluorides fuse easily and stick to the spoon. The final mass should be a loose crust which leaves the spoon easily. This operation takes about eight minutes, and should not be hurried, as proper time must be allowed for the action of the melted ammonium fluoride before it is driven off. It is well to use rather more than less of the reagent.

The residual fluorides are removed to the agate mortar, and well mixed with two full spoons of calcined sodium carbonate (say four to five times the weight of original mineral), and made to a paste with drop of distilled water. This paste is taken on loop of platinum wire and fused in strong blowpipe-flame, the beads being knocked off while liquid into a capsule, or on to the aluminium plate placed under the lamp. About four good large beads will result. The fusion must be at a very strong heat, and be kept up till some little time after all effervescence ceases in the bead. The mixing with sodium carbonate and fusion take eight to ten minutes.

The beads are then broken in the steel mortar, powdered in agate mortar, and the powder put into small test-tube and boiled with distilled water. Solution is very rapid, and so also is filtration. Subsequent operations need no further description. The water used is only a small quantity. Three little filters are required.

The whole analysis takes barely half an hour up to the precipitation of calcium oxalate, when of course the necessary time must be allowed before proceeding to test for magnesia. Thus caustic potash is no longer required, much less acid is used, and much less ammonia. Four small test-tubes are used supposing Ba and Sr absent, and their occurrence is rare in mineral silicates. I myself prefer this method even for silicates decomposable direct by acid.

I have given the above in some detail for the benefit of such mineralogists as are not specially chemists, and so may not be acquainted with the use of ammonium fluoride. This reagent must be pure of course, viz., it must leave no residue whatever when evaporated off platinum. It can be kept any length of time in glass bottles coated with paraffin wax.

While on the subject of blowpipe analysis perhaps I may be permitted to allude to a reagent I myself suggested several years ago, viz., the mixture of cuprous iodide and sulphur in place of Von Kobell's mixture of potassium iodide and sulphur.

The use of this mixture in connection with aluminium plate has proved itself most valuable as a delicate test for small amounts of Bi and Pb. What I wish to say is, principally, that when I first used it I had some doubts as to its retaining its efficiency for a long time. I have recently opened a case containing some reagents packed up for many years during my absence abroad, and I find some of the iodide mixture as good as the day I prepared it.

The same applies to some "Turner's flux" (for testing for boric acid in minerals) made many years ago. Dr. Iles, in writing of his use of glycerin as a test for boric acid (CHEMICAL NEWS, July 28th, 1877), said that Turner's reagent would not keep. It keeps perfectly if well stoppered, and if prepared as dry as possible. The glycerin test is a very neat and effective one. There is nothing to choose between it and Turner's test as regards delicacy. But glycerin is a nasty sticky mess to carry in one's reagent-case compared with Turner's reagent! There is, however, one case in which glycerin can be used where Turner's test is not applicable, viz., in the presence of copper. Using Turner's mixture, a volatile copper fluoride is formed which colours the flame strongly

green. Glycerin does not produce any such effect, of course, on copper compounds, and the boric combination volatilised is very distinct if properly introduced into the flame. Should the substance contain so much copper that it gives a green colour *without* glycerin, a little sodium carbonate should be added to the paste, sufficient to enable the Na colouration to overpower the copper-green. The boron-green will appear quite distinctly in spite of the sodium. A similar use of sodium-flame to cover the copper, with Turner's test, is not applicable, because the copper fluoride is quite as volatile as the boric combination, and appears, like that, in spite of sodium.

Chester, September 25, 1886.

ON THE
SEPARATION OF SILICA IN THE ESTIMATION
OF MANGANESE IN PIG-IRON,
AND ON THE
ESTIMATION OF PHOSPHORUS IN PIG-IRON
AND STEEL.

By L. MANDEVILLE DEANE, F.C.S.,
Sir W. G. Armstrong, Mitchell, and Co.

Estimation of Manganese.

THE methods commonly in use for the estimation of manganese in pig-iron are no doubt well known to most analysts who are engaged in iron and steel work, but I believe it is not generally as well known that the ordinary process requires modification where it is applied in the analysis of pig containing above 2 per cent of silicon, as is generally the case with hematite iron, in which as high a percentage as 4 per cent is often found.

Having had several years' experience in the analysis of the above-named substance, I have generally found that a very appreciable quantity of silica is apt to escape filtration, and is finally precipitated and weighed with the oxide of manganese, thus rendering the manganese estimation erroneous.

In lately analysing a sample of pig-iron containing 2.106 per cent of silicon, I found that 0.240 per cent of silica was precipitated with the oxide of manganese, thus making a considerable error in the determination of the manganese.

The process I made use of was as follows:—

Two grms. of the substance are dissolved in a flask by the addition of 1 fluid oz. of hydrochloric acid; when solution is effected $\frac{1}{2}$ a fluid oz. of nitric acid is added, and the heating continued until the red fumes have ceased to be evolved.

The solution is then poured into a large beaker, and largely diluted with boiling water; solid ammonium carbonate is now added, in small quantities at a time, until a deep mahogany colour is produced (the liquid being stirred round during the addition of the ammonium salt). As soon as this has occurred ammonium carbonate solution is dropped in until a slight permanent precipitate is obtained; after the addition of 4 fluid ozs. of strong ammonium acetate solution and stirring up, the beaker is heated until the contents boil briskly.

The beaker is then wrapped in a piece of felt, to prevent loss of heat as much as possible, and allowed to stand until the precipitated basic acetate of iron has settled. The solution is filtered through a large English filter-paper (glass rods being hung on the inside of the funnel to ensure greater rapidity of filtration); the precipitate is washed three times by decantation, which is easily done as the acetate settles very readily: at the third and last washing both the precipitate and solution are poured on the filter.

The large solution is now evaporated down in a porcelain basin to as small a bulk as possible; it is then

filtered through a Swedish filter, and the filtrate collected in an ordinary triangular flask; after the addition of bromine to slight supersaturation, the solution is allowed to stand for an hour or so.

Ammonium hydrate is next added with caution to excess, and the flask boiled; the hydrated oxide of manganese is collected on a washed Swedish filter, and washed once with hot water.

Both the filter and precipitate are dried; then ignited in a weighed platinum crucible, in a Fletcher's muffle-furnace, for about three-quarters of an hour.

On weighing the resultant precipitate, which should have consisted wholly of manganoso-manganic oxide, I found that it gave a higher percentage of manganese (viz., 1.490) than my experience led me to anticipate could have been present in the metal; I therefore concluded that there must have been some other substance mixed with the oxide, which substance I inferred to be silica.

I therefore brushed the oxide of manganese, &c., out of the crucible into a small beaker, and effected solution of the manganese by heating with a little hydrochloric acid; the insoluble residue (which proved to be silica) was collected on a washed Swedish filter, and washed three times with hot water, and the filter and silica ignited in a platinum crucible.

On weighing I obtained the following results:—

Silica = 0.240 per cent.

Manganese weighed and calculated (without subtracting the silica) = 1.490 per cent.

Manganese (silica being subtracted) = 1.318 per cent.

Difference between the two results = 0.172 per cent.

The second result therefore gives the correct amount of manganese in the pig-iron in question.

I proved that the large quantity of silica (which was precipitated with the oxide of manganese) did not come from the reagents used in the determination, by taking a steel containing 0.526 per cent of manganese and 0.138 per cent of silicon (a Siemens-Martin steel which was rather high in silicon). I found, in case of the above steel, that only 0.015 per cent of silica was precipitated with the manganese (this might proceed from an unavoidable amount present in the reagents, or from the glass vessels themselves): this would only make the result too high by 0.011 per cent—an insignificant weight in the determination of manganese.

Estimation of Phosphorus.

I have had a large experience in the estimation of the above impurity.

Having found in this determination that when the precipitation of the phosphorus was effected in a strong nitric acid solution and filtered in this condition, the precipitated ammonio-phospho-molybdate had a great tendency to pass partially through the filter, I proceeded as follows:—

Before adding the ammonium molybdate I diluted the nitric acid solution with cold water to about one-third the capacity of the beaker used. On filtering I found that a perfectly clear filtrate was invariably the result. I use the following process for the estimation of phosphorus:—

One gm. of the substance is dissolved in 20 c.c. of nitric acid (1.2 sp. gr.), and the solution taken to dryness; the dry residue is re-dissolved in hydrochloric acid, and the liquid again evaporated to complete dryness.

Solution is now effected in hydrochloric acid, and the silica separated by filtration.

The solution is then taken down nearly to dryness (until a skin has formed on its surface), a few drops of nitric acid are added, and heating continued until the red fumes have escaped. The solution, after cooling, is diluted with cold water to about one-third the capacity of the beaker, and, after the addition of 1 fluid oz. of ammonium molybdate solution and shaking up, the beaker is allowed to stand until the precipitation of the phosphorus

complete: this usually takes place in from one to three hours (very often in the former space of time).

As much as possible of the clear supernatant solution is poured off, and the precipitate is collected on a Swedish filter (which has been previously dried and weighed in a small glass weighing-bottle, provided with a glass stopper), and washed six times with cold water containing 1 per cent of nitric acid. The precipitate and filter are dried in a water oven for three or four hours, and weighed when cool.

The result of this weighing—the weight of the bottle and filter being subtracted—gives the amount of dried ammonio-phospho-molybdate, which is then calculated into phosphorus.

INDEXING CHEMICAL LITERATURE.*

REPORT OF THE COMMITTEE.

In presenting their Fourth Annual Report the Committee is pleased to record gratifying evidences of a wide and growing interest in the bibliographical work which it is designed to encourage and aid. During the past year the correspondence conducted by the Chairman has been three-fold greater than in any previous year, and the subjects referred to the Committee have increased in diversity much beyond expectation, until they include important questions in general chemical bibliography. Some of these questions pertain to matters which require for their solution an authority which the Committee is unwilling to claim or assume; such, for instance, is the question of uniformity in abbreviations of chemical periodicals, the desirability of which is admitted, while the feasibility of devising a list of abbreviations which would be regarded as authoritative is doubtful. One of the Committee discusses this subject in a communication to the Chemical Section, appended to this Report, and to this we relegate further consideration.

Indexes Published.

"Bibliography of Petroleum," by Prof. S. F. Peckham. Report on the Production, Technology, and Uses of Petroleum and its Products. Report of the Tenth Census of the United States, vol. x., 1884, 4to., pp. 281-301. [A comprehensive bibliography of Bitumen and its related subjects.]

"Bibliography of the Metal Iridium," by Nelson W. Perry, in Prof. W. L. Dudley's paper on Iridium published in "Mineral Resources of the United States," calendar years 1883 and 1884. Washington, 1885. 8vo.

"An Index to the Literature of Uranium, 1789 to 1885," by H. Carrington Bolton. *Smithsonian Report for 1885*. Washington, 1885. 36 pp., 8vo.

It is almost superfluous to call attention to the following superb work, yet for sake of completeness it may be here recorded:—

"Melting- and Boiling-Point Tables." Physico-Chemical Constants, by Thomas Carnelley. Vol. i., London, 1885. 350 pp., royal 4to. [To be completed in two volumes comprising about 50,000 melting- and boiling-point data.]

Reports of Progress.

Prof. William Ripley Nichols has done a great deal of work on the Index to Carbon-Monoxide, but defers printing another year.

Prof. Charles E. Munroe reports he is ready to print a section of his extensive Index to the Literature of Explosives.

Prof. L. P. Kinnicutt is engaged on a Bibliography of Meteorites.

Dr. F. E. Engelhardt is compiling an Index to the Literature of Common Salt.

Projected Bibliographies.

Prof. F. W. Clarke has nearly ready for the press a new edition of his "Specific Gravity Tables," Constants of Nature, Part I. This edition will contain about twice as much matter as the original work, although melting- and boiling-points are omitted, these having been catalogued by Dr. Carnelley in the work above mentioned.

Profs. William Ripley Nichols and Lewis M. Norton are engaged on a "Dictionary of Chemical Synonymes," which will prove a valuable contribution to chemical bibliography and of practical utility to chemists.

Mr. S. P. Sharples, of Boston, informed the Committee in November, 1885, of his willingness to complete an "Index to the Literature of Milk Analysis" which he had compiled several years before; and a few weeks later Mr. Clement W. Andrews, of the Massachusetts Institute of Technology, notified the Committee of a similar undertaking which he proposed perfecting and bringing down to date. These two gentlemen were at once put into communication, and a mutual understanding has been reached whereby useless duplication will be avoided.

Prof. Stephen F. Peckham, of Providence, R.I., whose voluminous "Bibliography of Petroleum" is noticed above, is engaged on a continuation of the work, which he plans to bring down to 1890.

Prof. William H. Seaman, of the U.S. Patent Office, calls attention to the important literature of Chemistry found in Patent Specifications, and proposes to compile an "Index to American Chemical Patents," for which undertaking he has unusual facilities.

Prof. Erastus G. Smith, of Beloit, has begun an "Index to the Literature of Aluminium," a topic suggested by the Committee.

Mr. George F. Kunz, of Hoboken, is collecting and indexing works relating to "Gems and Precious Stones." His bibliography already numbers 2000 titles, and will treat of the subject in a comprehensive manner, including facts relating to the history, mining, cutting, uses, and literature of gems in all languages.

Mr. William Beer, late of the College of Physical Science, Newcastle-on-Tyne, availing himself of facilities afforded by the Library of the University of Michigan, is engaged on a "Bibliography of Scientific Bibliographies," the first part of which he intends soon to offer to the Committee; he has also in an advanced state a "Bibliography of Copper."

The Committee desires to record thanks to the American Association for the Advancement of Science for reprints of reports furnished free of charge, and also to the Smithsonian Institution, which gratuitously distributed the reports to chemists and others.

The Committee again appeals to chemists for support, and calls for volunteers to undertake indexes to special topics in chemical literature, especially the chemical elements. The Committee dictates no fixed plan, but leaves method and subject to authors; the Committee does not seek to control the productions further than to insure work of high merit and to guard the interests of the Smithsonian Institution, which has agreed to publish manuscripts endorsed by the Committee. Sample copies of Indexes and other information can be obtained by addressing the Chairman, care of the Smithsonian Institution.

H. CARRINGTON BOLTON, *Chairman*.
IRA REMSEN.
F. W. CLARKE.
ALEXIS A. JULIEN.

July, 1886.

NOTE.—Since writing the above the death of Prof. Wm Ripley Nichols is announced. Absence from the country has prevented Prof. Albert R. Leeds from signing the above Report.

* Read before the Chemical Section of the American Association for the Advancement of Science, August, 1886.

NOTICES OF BOOKS.

President's Address. By Professor LIVERSIDGE, F.R.S.
Delivered to the Royal Society of New South Wales,
May 5, 1886.

THIS address contains much matter of very general interest. The position of the Society appears to be scarcely so desirable as the friends of science might wish. The number of Fellows does not increase and the debt on the Society's house is still not wiped out. Until this is done the Society cannot itself publish its annual volume of transactions. Important additions have been made to the library, the Council wisely turning its attention to obtaining complete sets of the Transactions of learned Societies, which are day by day becoming more rare and difficult to consult. During the past year only twelve papers have been read at the Society's meetings, two of which, moreover, were devoted to flying-machines! Three papers, however, have been read before the Microscopical and eighteen before the Medical Section.

Professor Liversidge very naturally complains that the number of original papers contributed to the Society is so small. Out of nearly 500 members, only 35 have contributed papers, and of these the majority have been furnished by some seven or eight individuals. He declares that "up to the present but little original work has been done in working out the chemistry of our mineral and vegetable products, and really but very little in many branches of biology." To account for this neglect he states that "There are but few men of leisure in the Colonies, and still fewer of learned leisure." Yet we have heard the complaint raised that in Australia there was nothing for young men of wealthy families to do, and that, consequently, many were drifting into dissipation!

There prevails, it would seem, a difficulty in obtaining gums and resins *true to name*, and this the President regards rightly as an additional proof of the ignorance (or indifference) which exists with regard to the natural products of the colony.

The Society offers its medal and a premium of £25 for original researches on a number of interesting questions. The papers due for May 1 this year included investigations on the chemistry of the Australian gums and resins, on the tin deposits of New South Wales, and on the iron ore deposits of New South Wales. The following are due on or before May 1, 1887. "On the Silver Deposits of New South Wales" and on "Origin and Occurrence of Gold-bearing Veins and associated Minerals." An investigation on the "Chemical Composition of the Products from the Kerosene Shale of New South Wales" is required by May 1, 1888.

An unpleasant fact here put on record is that the Biological Laboratory at Watson's Bay—a true aquarium—has been closed! Only one naturalist, and he a foreigner, has made use of the establishment!

This naturally leads Professor Liversidge to turn to the question of scientific training. He quotes largely and appositely from Prof. Huxley and Mr. Herbert Spencer, and he adds the remark that in the ordinary classical and mathematical education the student's "powers of observation and of reasoning from such observations are entirely neglected and undeveloped." We need not, surely, express our entire concurrence. A denunciation of "cram" or of word-knowledge as distinguished from thing-knowledge naturally follows. But how is it that whilst "cram" is attacked on every hand, and whilst scarcely a voice is raised in its defence, it still maintains its ground?

The late meeting of the British Association at Montreal naturally suggests the prospect of future meetings in other colonies, and Australia, from its size and its importance, naturally puts in the first claim. That Professor Liversidge, like ourselves, holds such a step to be exceedingly desirable is evident. But he sees, in the way of realising

the project, certain grave practical difficulties which it would be idle to ignore. These resolve themselves substantially into the two considerations of time and money. He says:—"The necessary travelling expenses would considerably exceed the whole year's income of many—for the pursuit of Science is not a lucrative one, and as a rule its followers are poor." The expenditure of time, too, would be very important. The visit to Montreal was managed by the majority of the 800 to 900 who entered their names for the meeting in a month or six weeks. But a voyage to Sydney by the shortest route takes about six weeks, and if we allow a week only for the actual business of the Association and a fortnight for visiting places of interest in Australia, we shall have a total little short of four months! How many professors, editors of scientific journals, officials of museums, consulting chemists, electricians, &c., could afford such a holiday? Hence the speaker held it doubtful whether above 50 members of the Association would put in an appearance at Sydney. He therefore proposes, as an intermediate step, the formation of an Australian Association for the Advancement of Science, the first meeting of which might be held on the hundredth anniversary of the colony, when, he adds, "there will probably be an International Exhibition to celebrate that event." We can only hope that some more patriotic and useful method of celebrating the event may be devised.

Returning from this brief digression we notice that Prof. Liversidge proposes the division of the Association into ten sections. Most of these coincide with the sections of the parent Association, Section I (Literature and the Fine Arts), is an innovation, and, as far as we can judge from the career of the so-called "Literary and Philosophical" Societies of England, one not to be recommended. Among a people, educated as the British race has been, literature, wherever introduced, generally secures the lion's share of attention and means. Section F (Economic Science and Statistics) is a dangerous member, from its tendency to degenerate into politics. Hence its excision in the British Association has been repeatedly mooted, and is doubtless a mere question of time. If retained it might very well be included under J (Social Science). In all other respects we are most favourably impressed with the outline scheme of the Australian Association, as suggested by Prof. Liversidge, and hope that it may be carried into execution.

On the Spectra of the Gases and Vapours Evolved on Heating Iron and other Metals. By JOHN PARRY, F.C.S. Pontypool: Hughes and Sons. Printed for private circulation.

IN the introduction to this book, some of Professor Graham's results are commented upon, and it is stated that in the course of a research on the quantity and kind of gases evolved on heating iron and steel *in vacuo*, results very different from Graham's have been arrived at, and conclusions are formed of great practical importance to iron and steel makers, namely, that the presence of gases in iron and steel is very deleterious, and should be prevented if possible.

The pages following are a collection of notes and papers on gases evolved by various metals, principally iron, and a description is given of the apparatus used and its general arrangement, by which means a number of photographs of spectra were taken.

In the paper on the gases contained in coke the results of a number of experiments are given, and the author has found, contrary to the general opinion, that coal persistently retains hydrogen, even at very high temperatures.

The latter part of the book consists of a collection of 58 plates of photographs of spectra, with a short note describing each.

Chemists will appreciate the excellent collection of photographs at the end of the work, which makes this a

most valuable contribution to our knowledge of spectra, and the author deserves great praise for the careful compilation of the same.

CORRESPONDENCE.

MAGENTA *v.* FUCHSINE.

To the Editor of the Chemical News.

SIR,—Mr. Allen might learn from the epithets “kako-phonous” and “un-English,” which I applied in my last letter to the term “fuchsine,” that I am very far from retiring from my original position. The combination of letters “chs” is so unsuited to Englishmen that most horticulturists have now converted “fuchsia” into “fuschia,” as better expressing its ordinary pronunciation. The terms “rose-colour,” “cherry-colour,” and “plum-colour” have become established by a convention of more than a century; but “fuchsia-colour” is not so recognised. Neither florists nor dyers understand by it any particular tone. One of the latter fraternity said, when questioned, that fuchsia-colour might mean anything from a pale flesh to a deep purple. In most varieties, too, the calyx and the corolla differ, whilst even the latter is not self-coloured, and changes its hues progressively from first opening until it falls. Hence I submit that Messrs. Renard were guilty of a twofold *bêtise* in applying to rosaniline hydrochlorate a name taken from such a flower. I for one shall certainly not encourage the use of a name which the practical sense of our countrymen has led them to reject.—I am, &c.,

YOUR REVIEWER.

VEGETO-CHEMICAL CHANGES.

To the Editor of the Chemical News.

SIR,—From the frequency of the English mail delivery we now receive constant and regular supplies of the CHEMICAL NEWS: in the various numbers many descriptions of vegeto-chemical changes may be paralleled in New Zealand.

In the June number of the present year (CHEMICAL NEWS, vol. liii., p. 277) there is a note from Mr. Samuel Rideal “On the Blue Colouring-matter of Decaying Wood,” in which it is stated that nitrogen takes no part in the production of the colour.

The following instance of the appearance of a very beautiful blue bears evidence of the presence of cyanogen:—My children shaped from a pukatea tree (*Atherosperma Novæ-Zelandæ*) a canoe, which was floated in an extemporised lake formed by the damming of a small stream. During the winter months no change in the colour of the water that occasionally leaked through the canoe was observed, but during the summer—when the water at a higher temperature had become surcharged with CO₂ from decaying vegetable matter—iron, which is so abundant in these volcanic soils, was dissolved, so that when the canoe was for any length of time filled with the water a beautiful deep blue colour was visible. After about two years the timber ceased to yield the same result.

A bushman, in occupying a new country, will select the neighbourhood of a pukatea as a fertile spot.

The Maoris make use of the bark of this tree as a nerve tonic. In the selection of a tree for stripping they always take one that has been exposed to the fullest effects of the sun's rays. I have succeeded in isolating an alkaloid from the bark in acicular crystals: a very small fragment placed on the tongue produced an intense bitter taste, which on passing away left a glow throughout the whole system that was felt for hours.

In a small case of preparations from our forest trees, sent to the Colonial Exhibition, there are some small

bottles of an extract formed from the bark of the pukatea tree.—I am, &c.,

W. IRWIN GRAYLING.

Egmont Village, New Plymouth, Taranaki,
August 6, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Biedermann's Central Blatt fur Agrikultur Chemie.
Vol. xv., Part 4.

Fluctuations of Carbonic Acid in the Air.—Prof. E. Wollny.—The author considers it highly probable that the quantities of carbonic acid produced by the industrial consumption of large quantities of fuel must produce a local augmentation of the proportion of this gas. The influence of putrefaction and decay seems to be only of subordinate importance. The ground-air is a productive source of carbonic acid. The air over fallow fields is richer in carbonic acid than that over land covered with vegetation. During the night the proportion of carbonic acid is greater than by day. The principal absorbents of carbonic acid are vegetation and the sea.

Processes of Oxidation and Reduction in the Soil effected by Microbia.—A. Müntz.—The author proves that the microbia are capable of oxidising or reducing certain haloid salts. The microbia of nitrification oxidise iodides to iodates and bromides to bromates. The experiments with chlorides have yielded no decisive results. In the absence of air potassium iodate was reduced to potassium iodide, and similar results were obtained with potassium bromate and chlorate.

Researches on the Capacity of the Soil for Water.—Prof. E. Wollny.—The conditions which have the greatest influence upon the capacity of a soil for water are the fineness of its constituents, their porosity, and the manner of their arrangement. The fertility of a soil cannot be determined by its capacity for water alone.

Experiments on the Cultivation of Beets in Posen.—Haake and Tschuschko.—Not susceptible of useful abridgment.

Ammonia or Chili Saltpetre.—Prof. W. Märcker.—In experiments on barley the effect, as compared with that obtained by a corresponding quantity of soda-saltpetre, was as 3 : 3.74 for the grain, and as 3 : 6.04 for the straw. Sulphate of ammonia does not give satisfactory results if used along with farm-yard manure. When nitrogen in sulphate of ammonia is used in place of nitrogen in soda-saltpetre, the quantity must be increased as 3 : 4 or at least 3 : 3.5.

Manurial Value of Bracken (*Pteris aquilina*).—R. Hornberger.—The value of the dried bracken from one hectare of land may be valued at 3rs. 6d.

Should Commercial Manures be dug in or scattered over the Surface.—Jul. van der Berghe.—The best result was obtained when the manures were dug in to the depth of 22 centimetres.

The Essential Chemical Elements of Plants.—T. Jamieson.—From the CHEMICAL NEWS.

Loss of Oxygen sustained by Plants in the Micro-spectrum.—N. Pringsheim.—There is no relation between the emission of oxygen and the absorption of light in the chlorophyll. The red rays between B and C do not especially subserve the decomposition of carbonic acid.

Oxalic Acid in the Vegetable World.—Berthelot and André.—From the *Comptes Rendus*,

Action of Chlorophyll and Carbonic Acid outside the Vegetable Cell.—P. Regnard.—From the *Comptes Rendus*.

Respiration of Leaves in Darkness and the Carbonic Acid retained by Leaves.—Dehérain and Maquenne.—From the *Comptes Rendus*.

Effect of Saline Solutions upon the Germination of the Seeds of Certain Indigenous Crops.—M. Jarius. Weak solutions of the salts used in agriculture, from 0.4 to 1 per cent, favour germination and subsequent development, whilst solutions containing 2 per cent depress both.

Part ascribed to the Living Tissues of Wood in the rising of the Sap.—J. Vesque.—From the *Comptes Rendus*.

Exsiccation of Plants in Aqueous Saline Solutions.—A. Levallois.—From the *Comptes Rendus*.

Presence of Methylic Alcohol in the Products of the Distillation of Plants with Water.—Maquenne.—From the *Comptes Rendus*.

Composition of Capsicum Annum.—F. Strohmer.—Analysis of the entire fruit, of the seeds, and of the husks.

Valuation of American Red Clover.—Dr. Troschke.—The composition of American clover does not greatly differ from that of Silesian and Italian clover.

Experiments on the Cultural Value of Different Kinds of Oats.—O. Bessler and Prof. M. Maercker.—The results are given in the form of tables.

Preparation of Factitious Fatty Cheeses.—Dr. v. Klenze.—Rich cheeses of good quality cannot be produced by the addition of foreign fats.

Influence of Sunlight on the Vitality of Microbia.—E. Duclaux.—From the *Comptes Rendus*.

Fermentation-Products of the White Grapes of the Charente.—Ch. Ordonneau.—From the *Comptes Rendus*.

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Justus Liebig's Annalen der Chemie,
Vol. ccxxxiv., Part 2.

Communications from the Chemical Laboratory of the University of Jena.—These consist of memoirs by Dr. A. Hand on certain benzol derivatives, and by Dr. Ad. Isbert on acetacetic ether and certain of its derivatives. The former of these papers treats of the so-called "fourth" monobromphenol, of the diazo-compounds, and of the question of metamerism in benzol. Dr. Isbert discusses the action of alcoholates upon acetacetic ether, the amide of ethyl-acetacetic ether soluble in water, the behaviour of phosphorus pentachloride with ethyl-acetacetic ether and with the corresponding methyl-compound, the action of sodium ethylate upon mono-chlor-ethyl and methyl-acetacetic ethers, and the decomposition of ethoxyl-alkyl-acetacetic ether by sodium hydroxide.

Investigations on the Glycidic Acids.—P. Melikoff.—The author concludes that although the glycidic acids belong to the saturated compounds they possess the property of direct addition. The energy of hydration decreases with the increase of the molecular weight. Isomeric acids vary in their capacity of hydration, which depends on their constitution. Those acids in which oxygen is combined with a tertiary atom of carbon possess a relatively greater energy of hydration. The haloid acids combine as energetically with the higher as with the lower members of the series. The elements of ammonia combine with the glycidic acids, forming amido-oxyacids.

Communications from the Chemical Laboratory of the University of Geneva.—These comprise a paper by L. Gresly on the reduction and condensation of the homologues of benzoyl-benzoic acid, and a notice, by the same author, on the formation of triphenyl-methan-carbonic acid from phenyl-phthalide.

On Lactucine.—O. Hesse.—The author describes two compounds, α - and β -lactucol, which he obtains from lactucine.

On Pseudomorphine.—O. Hesse.—The author describes some reactions by which pseudomorphine and morphine are distinguished. Morphine dissolves in pure strong sulphuric acid with a faint reddish colour. Pseudomorphine dissolves at first colourless, but the solution soon becomes yellowish and then reddish. If the acid contains a very little ferric oxide morphine gives a reddish solution, but pseudomorphine a fine blue, which soon turns an intense violet and finally a brownish green. If morphine is mixed with an equal weight of cane-sugar it dissolves in sulphuric acid (pure or containing ferric oxide) with a violet-red colour. Pseudomorphine under the same circumstances yields, with pure sulphuric acid, an intense dark green, turning olive. If the acid contains ferric oxide the colour is at first a splendid blue, turning subsequently to an intense dark green.

Part 3.

Specific Heat of Homologous Series of Liquid Carbon Compounds.—Robert Schiff.—The author's results are given in the form of tables.

Evaporation-Heats of Homologous Carbon Compounds.—R. Schiff.—This memoir, which, like the foregoing, requires the accompanying figures, does not admit of useful abstraction.

On the Carbohydrates.—O. Wallach.—The author has examined a carbohydrate occurring in the rhizomes of the sweet-flag (*Iris pseudacorus*). It is more powerfully lævo-rotatory than inuline. It does not reduce Fehling's solution, but is rapidly converted into sugar by dilute acids. It is much more soluble in cold water than inuline, and in the sections of the rhizomes it has not been found practicable to produce the double refractive spherocrystals so characteristic of inuline. Hence the author concludes that this product is not identical with inuline, in spite of many points of resemblance.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1402.

DISSOCIATION AND CONTACT-ACTION.*

By the Rev. A. IRVING, B.Sc., BA., of Wellington College.

IN a letter which appeared in *Nature*, on the 25th of March last, the author referred to some recently-published work of M. Konovaloff on Contact-action Phenomena, and to the suggestion thrown out by that gentleman that the bombardment of the molecules on the solid matter might cause a transformation in part of their kinetic energy into intramolecular work, tending to bring about dissociation of the molecules. Getting no reply to his request for information as to any previously-published work on this subject, and having found that one or two eminent chemists to whom he has mentioned the subject took a favourable view of the theory, which he has for some years past pointed out to his more advanced pupils as probably the true explanation of the experimental results observed, when, under the influence of heated spongy platinum or platinised asbestos, or other porous or finely-divided bodies,† combinations are brought about with the intervention of contact-action at much lower temperatures than are required without such contact-action, the author has ventured to bring the subject up for discussion in this Section.

Some of the most familiar examples of this kind of action are the following:—

- (1.) The oxidation of ammonia, and of SO_2 in the presence of an excess of O_2 .
- (2.) The conversion of nitric oxide into NH_3 and H_2O in the presence of an excess of H_2 .
- (3.) The direct combination of mixtures of H_2 and Br_2 , and of H_2 and I_2 respectively.
- (4.) The oxidation of NH_3 gas, and of the vapours of alcohol and ether, by atmospheric oxygen in contact with a glowing coil of platinum-wire, or of a heated glass rod.

Of the explanations of these and similar phenomena which the author has met with, the following require a passing notice:—

1. The antecedent formation of a hydride with the hot metal, as when H_2 is passed over red-hot palladium; or the absorption of H_2 , which is known to occur in the case of red-hot platinum to the extent of 3.8 times its own volume (Roscoe and Schorlemmer, II., ii., p. 397). This may explain the rekindling of a Bunsen gas-jet by a heated mass of spongy platinum, or even by heated platinum-foil, on account of the large quantity of free H_2 present in coal-gas, but it manifestly cannot apply to such instances as the oxidation of ammonia or sulphur dioxide by contact-action, and of course fails to apply to any case in which some other porous body is substituted for platinum.

2. Oxygen, it is well known, is condensed on the surface of cold platinum to such a remarkable extent that a large coil of platinum-foil, after considerable exposure to the air, may be buoyed up, so as to float in water, by the bubbles of oxygen which collect on its surface under the exhausted receiver of an air-pump. This condensation of O_2 on the surface of cold platinum is the probable cause of that increased activity which enables it to act

spontaneously upon the jet of hydrogen in Döbereiner's lamp; but it fails to explain such instances of contact-action as we are considering, for (a) the oxidation of SO_2 or NH_3 in the presence of an excess of O_2 does not appear to be brought about by contact with cold platinum sponge; (b) it has no application in the case of the combination of NO and H_2 .

3. To say that the gases are "encouraged" (as is said in at least one text-book) to combine, by the hot metal, is a mere metaphorical blind, and altogether unscientific.

Other substances besides finely-divided platinum are known to effect similar changes, when they are heated, by mere contact action, though in a less marked degree. We must seek therefore in another direction for an explanation which shall include all the known instances, and this may perhaps be found in those *thermo-dynamical principles which underlie the kinetic theory of gases*.

Proposed Theoretical Explanation of the Phenomena.

Starting with the law that the kinetic energy of a gas is proportional to its absolute temperature, and with the view that the total resistance of a gas is the sum of the energies of motion of its constituent molecules, it does not follow that this energy of motion is *the same in all the molecules*; the temperature indicated by the thermometer must rather be regarded as the mean of the temperatures (energies of translation) of the molecules. This would seem to follow from a consideration of the fact that during infinitely short periods of time the motions of individual molecules proper to their absolute temperatures must be affected as regards their intensity (velocity) by mutual impact, as is the case with all elastic bodies; also from the further fact that the effect (as regards energy of translation) of the impact of individual molecules against the rigid walls of the containing vessel cannot be the same as that resulting from their mutual collision. Again, since a molecule has weight, the energy of translation of each molecule must be slightly affected by gravitation, according as it is pursuing an ascending or descending path with reference to the Earth, though the number of ascending and descending molecules being equal, this does not interfere with the equality of tension of the mass of the gas upon all parts of the enveloping surface. These considerations would seem to hold good in a gas (or mixture of gases) at constant temperature,—that is to say, when there is no measurable accession of heat to, or withdrawal of heat from, the system. While, however, heat is being applied to the system from without, or withdrawn from it, the variations of the energy of translation of the individual molecules will be much greater.

Further, the atoms themselves must be regarded as carriers of dynamical energy, and with variations in the heat energy (absolute temperature) of the free molecules there must be variations also in the intensity of the energy with which the variations of the atoms take place within the molecules; in other words, there must be variations in the atom-temperatures along with variations in the energy of translation of the molecules themselves. The different degrees of stability of molecules of different kinds is thus seen to be accounted for by the different ranges of what we may call the *fields of intensity of the chemical affinity* which the constituent atoms (or radicles) possess for one another: the more intense their mutual attraction, the wider is the range within which the vibratory motion (atom-temperature) may increase without the atoms themselves passing beyond that range, or becoming *dissociated*.

"Dissociation-temperature"—so far as individual molecules are concerned—may be taken, then, to represent simply a sufficient increase in the vibratory motions of the atoms to carry them beyond the range of the attraction of affinity which holds them together in the molecule. Now since both the energy of translation of the molecules and the atom-temperature vary within wide limits, it follows that in a given mass of gas there must be some molecules which require a smaller accession of heat from

* Read before the British Association, Birmingham Meeting, Section B.

† The author has obtained very marked results with pumice-fragments (previously well calcined) for $\text{SO}_2 + \text{O}_2$, both well dried ($2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$). He has also obtained less marked, but quite distinct, traces of oxidation of NH_3 with heated pumice-fragments, as explained in the text of the paper when spongy platinum is used.

without the system than is required by those which are in the condition of the mean dynamical intensity of the system, in order that they may be dissociated. This is what is known as the *initial temperature of dissociation*.

If the mean temperature of the system be maintained constant above that of the initial-temperature of dissociation, a certain percentage of the gas will be dissociated, the percentage varying with the excess of the absolute temperature of the system over that of initial dissociation. For the same temperature (other things being equal) the same percentage of the gas is dissociated, but not the same identical molecules; new molecules are continually undergoing dissociation, while some of the previously dissociated atoms, owing to diminution in the intensity of their vibratory motion, enter again into molecular union; so that for complete dissociation one of two things is required,—either the removal from the system of the isolated atoms (at least of one kind) as fast as they become dissociated, or an enormous elevation of temperature of the whole system.

An illustration of this principle is furnished by the case of steam, which begins to undergo dissociation (at a pressure of about one atmosphere) at a temperature somewhere between the melting-points of silver and platinum, since a quantity of oxyhydrogen gas can be obtained by passing water-gas (H_2O) through a white-hot tube of platinum, or by dipping a white-hot ball of the same metal into water; that is to say, the initial temperature of dissociation lies between the melting-points of silver and platinum. Reflecting further on the fact that the intense heat of the oxyhydrogen blowpipe-flame is produced by the union of the two elements of water, we see that the temperature of complete dissociation of steam lies far above that of even the oxyhydrogen flame. As a corollary to this it follows that in the intensely hot inner flame of the oxyhydrogen blowpipe the oxidation of the hydrogen is not completed, some of the gases passing beyond it in the dissociated state, and uniting to form steam in the outer mantle of the flame, where the temperature is lower.*

Instances are well known to chemists in which an accession of heat to the system may result from a rearrangement of portions of the system, as when, on the initial temperature of dissociation being reached in a body of tolerably complex molecular structure, such as ammonium nitrate, the isolated atoms of oxygen and nitrogen on the one hand, and of oxygen and hydrogen on the other, though supplied with sufficient atom-temperature to remove them out of the range of the field of intensity within which, at lower temperatures, they were held together in the ammonium nitrate molecule, are yet only possessed of such a degree of intensity of vibratory motion as is well within the range of the field of intensity of the attraction of oxygen atoms for nitrogen atoms and hydrogen atoms respectively. Even if in this case we regard the nitrous oxide as merely a reduction product resulting from the action of nascent hydrogen furnished during the first stages of decomposition, the bearing of the facts upon our present investigation is the same; heat is generated within the system by the energy set free by the formation of molecules of steam, if not by the formation of molecules of nitrous oxide. Again, when oxyhydrogen gas, or a mixture of hydrogen and chlorine, is exploded, the initial dissociation produced by the spark-discharge enables the atoms of opposite electro-chemical energies to combine, and that with such a degree of energy as to affect very rapid dissociation of contiguous molecules followed by a cross combination of their atoms to form new molecules (steam or HCl , as the case may be); the heat of combination being so greatly in excess of that expended in dissociation, added to that which escapes from the system, that the degree of the intensity reached by the heat of the system is momentarily enormous.

In such a case as that of the combustion of a mixture of ammonia (a stable compound) and oxygen, this excess is comparatively small, and the rise of temperature of the system is so slow, that the progress of the flame through the mixture can be followed with the eye; while in the presence of a considerable proportion of an inert gas (such as nitrogen), which acts as a diluent, this excess becomes a negative quantity, so that atmospheric air does not support the combustion of ammonia.

Bearing all these considerations in mind it may not be difficult to see how the intervention of a porous or finely-divided solid, such as spongy platinum or platinised asbestos, may facilitate dissociation, and so start the combination of gaseous bodies, which in their free molecular state do not, under ordinary physical conditions, act upon one another. The enormous increase of the solid surface must lead to a corresponding increase of the number of collisions in a given time between the individual molecules and that surface; and the consequence of this may be (and probably is) that internal work is done among the atoms of the molecules by increasing the intensity of their vibratory motion. It would result from this, that, so far as the molecules thus affected were concerned, a smaller accession of heat from without the system would be necessary to bring about initial dissociation; that is to say, the initial temperature of dissociation would be lower than without the intervention of the finely-divided solid body. So much for the "bombardment of the molecules against the solid surface." It is even conceivable that in certain cases the molecules may be so unstable that the intervention of the finely-divided solid may be a sufficient agency (without any addition of heat externally to the system) to cause the initial-temperature of dissociation to be reached.

Those who have repeatedly performed the experiments in the cases mentioned in the early part of this paper will probably have noticed (in the case of the oxidation of SO_2 , for example, by contact action) that the action begins at first very slowly and increases in intensity as it proceeds, as if from the accumulation of heat from within the system, the energy of combination of SO_2 and O being probably greater than that required to dissociate wholly or partly the antecedent molecules. In the oxidation of NH_3 into nitric oxide and steam (disregarding the further action of these bodies on one another and on the residual ammonia and oxygen present), a higher initial temperature is found to be necessary, as the result of the greater solubility of the NH_3 molecule.

There are two or three considerations not to be overlooked.

(1) In the case of stable gases, such as NH_3 or NO , the experiment only seems to succeed when there is a large excess of the other body, which is more easily dissociated— O_2 in the one case, H_2 in the other; the presence of the greater number of dissociated atoms thus secured increasing the chances of their intervention under suitable conditions between the comparatively few dissociated atoms of the more stable gas before these re-combine, as their temperature falls, while they are carried on and away from the contact influence. An example of something analogous to this is seen in the five different nitrogen compounds obtained by the action of zinc (and some other metals) on nitric acid of different degrees of density.

(2) The action goes on more rapidly (within limits probably determined by the stability of the resulting compounds) as the temperature of the solid body is raised, as if the increased radiation from the powerfully radiating surface of the porous body helped to increase the vibrations of the atoms and so to facilitate dissociation.

(3) Reflecting upon the viscosity or internal friction of the molecules of a gas (or mixture of gases), may we not ask whether the introduction of the porous or finely-divided solid in our experiments may not lead to the substitution of friction of molecules against the solid surfaces for friction of the elastic molecules against one another to such an extent that it plays an important part, when

* Vide Wislicenus, *Kurzes Lehrbuch der Anorganischen Chemie*, § 104.

transformed into intramolecular work, in promoting dissociation?

The Quasi-nascent State.

By this term, which the author is in the habit of using, is meant that there is not probably actual dissociation in all the molecules which take part in the reaction (though there may be in some of them); but the intramolecular work done upon the atoms produces such a tendency towards or near approximation to dissociation, that when molecules in such a state of tension (if the term may be allowed) approximate in space sufficiently to one another, the atoms of opposite electro-chemical energies in the two kinds of molecules can separate out from their original molecules under the influence of their mutual attraction, so as to unite to form the new compound. We may illustrate this very well by reference to more tangible examples; as (1) the rapid action of Cl_2 upon H_2O , even without the aid of strong light (which is necessary for the production of free oxygen in chlorine water), when a reducing agent, such as SO_2 , is present; (2) the readiness with which NO_2 surrenders one of its oxygen atoms to SO_2 in the lead chamber. In both cases it would seem that the residual affinity of the sulphur-atom of the SO_2 is sufficient, when added to the counter-attraction of the Cl_2 in the first case and of itself in the second, to bring the oxygen atom out of the range of the field of the attraction within which it was previously held.

Collateral Evidence of the Truth of the Theory.

1. In a discussion in Section A last year Sir William Thomson said:—"If we take an absolutely elastic globe and cause it to rebound between two parallel and absolutely smooth planes in a region where gravity does not act, it will go on moving between the two. But he did not believe this would go on for ever. The translational energy of the ball will get transformed into higher and higher modes of vibration, so that at last the ball will come to rest, as it will be impossible for this energy to be transformed into translational energy." This is perhaps the clearest statement that could be made of the purely dynamical aspect of the cases we are considering; and a little reflection will show that this transformation would result (in the case of molecules) in the elevation of the atom-temperature or vibrational energy of the atoms; that is to say, energy of translation is partly expended in intramolecular work, which produces (or tends to produce) dissociation. In the case of a porous or finely divided solid we have not two parallel planes but an indefinite number of solid surfaces, multiplying indefinitely the frequency and number of instances of impact of the molecules upon the solid surface. This illustration enables us to understand the possibility, in some cases, of dissociation and consequent reaction between different kinds of atoms without any external application of heat to the system.

2. A reference must be made to Mr. Crookes's beautiful instrument—the Radiometer. The rotation of the vanes in this instrument is undoubtedly due to the difference of temperature of the polished and blackened surfaces of the plates, owing to the high degree of absorptive (and emissive) power possessed by the latter, and the high reflective power possessed by the former, for radiant energy; the result of which is that when radiation in excess is entering the instrument the temperature of the blackened surfaces is relatively raised by the greater degree of absorption, and, conversely, when radiant energy in excess is escaping from the instrument, the temperature of the blackened faces is lowered relatively by the greater degree of their emissive power, as compared with the highly-polished metallic faces of the plates. Action and reaction being always equal in quantity and opposite in direction, the rotation of the vanes must be directly proportional to the extent to which the energy of bombardment of the molecules of the highly-rarefied medium upon the blackened surfaces exceeds the energy of bombardment of the molecules upon the polished surfaces, when a positive direction of rotation is given to the vanes, or

falls short of it when a negative direction is given to them. It may not be easy to decide how far, in a highly-rarefied medium, the change in the force of the bombardment of the surface, whose temperature is slightly raised or lowered, is divided between a change in translational energy of the molecules and the additional *spring* which is given to the atoms themselves; but the fact is patent enough, even for changes of temperature which are almost infinitesimal as compared with the elevation of temperature produced from without in most of the experimental processes of the kind we are considering in this paper.

3. In a lecture given in May last, at the Royal Institution, Mr. Frederick Siemens showed that contact of a flame with highly-heated surfaces tends to *prevent the inter-combination of dissociated atoms*, with a corresponding loss of heating power in high-temperature furnaces. This is a result which we should expect to follow as a deduction from the theory advocated in this paper, if that theory is the true explanation of the facts; and these experimental results on a large scale may be accepted as evidence, while we regard the retardation of combination which he describes as following from the action of purely thermo-dynamical causes, rather than by supposing (as he does) that it is brought about by what he calls an "adhesive or condensing influence of surfaces on the atoms of the gas," for which there would appear to be no foundation either in thermo-dynamical principles or in experimental work, except in such very special instances as the formation of alloys of hydrogen with palladium or platinum.

The explanation offered in this paper of contact action as promoting combination between gases, which in the free state and under ordinary physical conditions do not act chemically upon one another, has at least the scientific merit of being applicable to *all* cases of the kind, which is more than can be said for any other explanation of the phenomena which has been offered hitherto. It has also, perhaps, the further merit of grouping together the chemical changes produced by the contact action of a solid, which takes no part in the chemical change itself, with those produced by purely physical agencies, as being all referrible to the same thermo-dynamical laws. Among the latter may be mentioned the combinations effected by the spark discharge, the silent electric discharge (as in the synthesis of NH_3), the continuous spark stream (as in the case of the oxidation of N_2 in dry air), and light (as in the synthesis of HCl). There is also, it will be seen, a considerable extension of our idea of the action of elementary atoms in the nascent state.

ON THE NATURE OF SOLUTION.*

By Professor W. A. TILDEN, F.R.S.

FOR want of time the consideration of various phenomena connected with the subject was necessarily omitted. Thus no reference could be made to the various formulæ relating to expansion or density of solutions, nor to their optical properties, magnetic rotation, nor to the subject of electrolysis.

In what follows a review is presented of the principal phenomena observed in the act of solution of solids (especially metallic salts and other comparatively simple compounds) in liquids, and the chief properties of the resulting solutions, with the object of arriving, if possible, at some conclusion as to the physical explanation of the facts. The question must at once arise whether these phenomena are to be considered as chemical or mechanical, and all the theories which have been put forward to explain the nature of solution are roughly divisible into

* Abstract of Opening Statement in the Discussion on the "Nature of Solution," British Association, Birmingham Meeting, Section B.

two classes, according as, on the one hand, they represent the process as a kind of chemical combination, or, on the other, explain the phenomena by reference to the mechanical intermixture of molecules or by the influence of the rival attractions of cohesion in the solid and liquid, and of adhesion of the solid to the liquid. The former hypothesis seems to have been universally adopted by the older writers, such as Henry and Turner, and it seems pretty clear that Berthollet also regarded solution as an act of chemical combination. Among modern chemists Professor Josiah P. Cooke takes a similar view. But M. Berthelot is the most consistent and powerful supporter of the same hypothesis. In his "*Mecanique Chimique*" (tome ii., p. 160) will be found a very clear and formal statement of his views upon this subject, which it is interesting to know are retained by M. Berthelot without modification in any essential particular.

On the other hand, there are a number of writers who—whilst referring the phenomenon of solution to a molecular attraction of some kind—do not attribute solubility to the formation of chemical compounds of definite composition. Graham distinctly ranges himself on this side; Brande also appears to have taken a similar view; and Daniell, Miller, Nicol, and Dossios may be more or less ranked with them. A theory differing in some important respects from those of the above writers was briefly enunciated in a paper communicated to the Royal Society by Tilden and Shenstone in 1883. In discussing the connection between fusibility and solubility of salts, the authors point out that the facts tend to "support a kinetic theory of solution, based on the mechanical theory of heat. The solution of a solid in a liquid would accordingly be analogous to the sublimation of a solid into a gas, and proceeds from the intermixture of molecules detached from the solid with those of the surrounding liquid. Such a process is promoted by rise of temperature, partly because the molecules of the still solid substance make longer excursions from their normal centre when heated, partly because they are subjected to more violent encounter with the moving molecules of liquid." This theory, however, only relates to the initial stage of the process of solution, and does not sufficiently explain saturation, nor the influence of dissolved substances upon vapour pressure, specific heat, specific volume, &c. How far is it true that evolution of heat indicates chemical combination? does the evolution of heat which often takes place on dissolving a solid in water, or on adding more water to its solution, indicate the formation of hydrates, *i.e.*, compounds of the dissolved body with water, in definite proportions? Thomsen answers this question in the negative (*Thermochemische Untersuch.*, iii., 20).

Take the case of sulphuric anhydride (SO_3). It is evident from the diagram exhibited that more than half the total evolution of heat occurs on addition of the first molecule of water to the solid substance; yet the succeeding molecules give quite an appreciable thermal change. At what point in such a curve should we be justified in setting up a distinction between the effect due to chemical combination and that due to other causes, such as the change of volume consequent on dilution, or the possible loss of energy from the adjustment of the motion of the molecules of the constituents to the conditions requisite for the formation of a homogeneous liquid, or (though not in the present case) the decomposition of the compound by the water?

In the act of solution of solids, and especially of anhydrous salts, in water, the volume of the solution is always less than the sum of the volumes of the solid and its solvent, with the exception of some ammonium salts in which expansion occurs. Similarly the addition of water to a solution is followed by contraction. This contraction may be due to mere mechanical fitting of the molecules of the one liquid into the interspaces between the molecules of the other (*see* Mendeleeff, Abstract in *Journ. Chem. Soc.*, February, 1885, p. 114). This would

probably not be attended by loss of energy. Or, again, the contraction may arise from the re-adjustment of molecular motion already referred to.

If we know the coefficient of expansion of the liquid and its specific heat, we can calculate the amount of heat evolved for a given contraction. If this is done for sulphuric acid, and many other cases, it is found that, after accounting for the thermal change due to alteration of volume alone, there is a surplus of heat evolved which may really indicate some kind or some amount of chemical combination.

Thomsen has found that, as a rule, the heat of solution and of dilution are both either positive or negative. Of thirty-five salts examined, only four supply well-marked exceptions.

However we may ultimately explain the anomaly exhibited by these salts, the fact remains that the heat evolved or absorbed during the admixture of any substance with water is in every case a continuous function of the quantity of water added. Similarly the contraction which ensues on diluting an aqueous solution proceeds continuously, and the molecular volume of a salt in solutions of different strengths is continuously greater the larger the amount of salt present. So that in none of these thermal or volumetric phenomena is any discontinuity observed, or any indication of the formation of compounds of definite composition, distinguishable by characteristic properties.

The question we are now considering, as to whether in a solution the solvent and the substance dissolved in it—or any portion thereof—exist independently of each other, is in some degree answered by the facts known as to the specific heats and vapour pressures. For instance, when water is added to a solution of sodium nitrate, the molecular heat of the resulting liquid seems to show that all the water added is influenced, at least until a very large quantity is present. In this case one molecule of sodium nitrate can affect the movements of 100 molecules of water, and probably more. It is also well known that the vapour pressure of water holding in solution almost any dissolved solid is less than the vapour pressure of pure water, and that the boiling-point of a liquid is raised by the addition to it of any soluble non-volatile substance. This fact of reduction of pressure can only be explained upon the hypothesis that there is no free water present at all; that is, that there is no water present which is not more or less under the influence of the dissolved substance. What becomes of water of crystallisation forms a part of the same question as to the relation of solvent to solvent. Observed facts lead us to conclude that white copper sulphate, blue anhydrous cobalt chloride,—and, by analogy, other salts which are colourless,—retain their hold upon the water of crystallisation when they are dissolved in water. A very important observation has been made by Dr. Nicol, which bears directly upon this question. In his study of the molecular volumes of salt solutions he finds that when a salt containing water of crystallisation is dissolved, this water is indistinguishable by its volume from the rest of the water of the solution. In the Report presented to the British Association last year the following passage occurs:—"These results point to the presence in solution of what may be termed the anhydrous salt, in contradistinction to the view that a hydrate, definite or indefinite, results from solution; or, in other words, no part of the water in solution is in a position, relatively to the salt, different from the remainder." These two statements, however, are not strictly consequent upon each other. The view seems preferable that (save, perhaps, in excessively dilute solutions) the dissolved substance is attached in some mysterious way—it matters not whether it be supposed to be chemical or physical—to the *whole* of the water. We cannot otherwise get over the difficulty presented by the hydrated salts which give coloured solutions, by the control of the vapour pressure by the dissolved salt, and by the altered specific heat. With regard to water of crys-

tallisation, E. Wiedemann has shown that hydrated salts in general expand enormously at the melting-point; and the observations of Thorpe and Watts on the specific volume of water of crystallisation in the sulphates of the so-called magnesium group show that—whilst the constitutional water occupies less space than the remaining molecules—each successive additional molecule occupies a gradually increasing volume. So that when a salt, with its water of crystallisation, passes into the liquid state (either by melting or by solution in water) it requires a very slight relaxation of the bonds which hold the water to the salt for it to acquire the full volume of liquid water, whilst the water of constitution is not so easily released. And this conclusion accords with Nicol's observations on the molecular volumes of the salts when in solution.

Now comes the question as to what determines the solubility of a substance. Why, for example, is magnesium sulphate very soluble in water, whilst barium sulphate is almost totally insoluble? With regard to salts the following propositions seem to be true:—(1) Nearly all salts which contain water of crystallisation are soluble in water, and for the most part easily soluble. (2) Insoluble salts are almost always destitute of water of crystallisation, and rarely contain the elements of water. (3) In a series of salts containing nearly allied metals the solubility and capacity for uniting with water of crystallisation generally diminish as the atomic weight increases. The fusibility of a substance has also much to do with its solubility. Neither fusibility alone nor chemical constitution alone seems to be sufficient to determine whether a solid shall be soluble or not, but it may be taken as a rule, to which there are no exceptions, that when there is a close connection in chemical constitution between a liquid and a solid, and the solid is at the same time easily fusible, it will also be easily soluble in that liquid.

Salts containing water of crystallisation may be considered as closely resembling water itself, and these are, for the most part, both easily fusible and easily soluble in water. But space is wanting for the discussion of the details of these matters, as well as the relation of molecular volume to solubility of solids.

The fascinating character of the phenomena of supersaturation has attracted a host of experimenters; but no definite explanation has been generally accepted. In the opinion of the speaker supersaturation is identical with superfusion. Supersaturated solution of (say) alum, thiosulphate of sodium melted in its water of crystallisation, and fused sulphur at 100° exhibit phenomena of exactly the same kind.

Finally, we are led to the consideration of what is meant by chemical combination. From the phenomena under discussion, and others, the conclusion seems inevitable that chemical combination is not to be distinguished by any absolute criterion from mere physical or mechanical aggregation; and it will probably turn out ultimately that chemical combination differs from mechanical combination—called cohesion or adhesion—chiefly in the fact that the atoms or molecules of the bodies concerned come relatively closer together, and the consequent loss of energy is greater.

WATER ANALYSIS.

THE following letter, addressed to Mr. Crookes, Chairman of the Chemical Section of the British Association for the Advancement of Science, arrived too late to admit of its being brought before the notice of the Section:—

SIR,—At the meeting, held this month, of the American Association for the Advancement of Science, a Committee was appointed to report a scheme, for general adoption, of stating the results of the analysis of waters, both potable and mineral.

The chief points to be discussed by the Committee are—

1. The scale upon which the results shall be given,—whether parts per 100, 1000, 100,000, or 1,000,000, or grains per gallon, &c.
2. The method of naming the constituents determined,—whether, for instance, in the case of a mineral water, the basic and acid substances shall be given separately, or whether the salts supposed to be present; or whether we shall say so much Na, K, Ca, Mg, S, as sulphate, &c.

As you are well aware, there is a great variety of methods of stating these results of water analysis, and the desirability of a uniform method cannot be questioned.

It was suggested in our Chemical Section of this Association, when this Committee was appointed, that perhaps the Chemical Section of the British Association might be willing to co-operate with us in this matter. To this end I lay the action of the Chemical Section before you, trusting that you will take such steps concerning it as may seem proper.

Our Committee reports a year hence, at the next meeting of the American Association. If this should reach you in season for any corresponding action by your Section, we should be pleased to be put in communication with the Committee appointed.—Yours respectfully,

G. C. CALDWELL,
Chairman of the Committee.

Chemical Department, Cornell University,
Ithaca, N.Y., August 28th, 1886.

A PROBLEM IN CHEMICAL BIBLIOGRAPHY.

APPENDIX TO REPORT OF COMMITTEE ON INDEXING CHEMICAL LITERATURE.

By H. CARRINGTON BOLTON.

IT IS no disparagement to the profession to say that not all chemists are bibliographers; the peculiar talents and skill which ensure success in laboratory researches have no necessary connection with the technical erudition of bibliography. In preparing for publication records of their researches, chemists generally aim to chronicle the previous labours of others in the same or analogous lines, but in quoting from periodicals the writers sometimes give little thought to their accurate and systematic designation. A lack of uniformity is especially marked in the abbreviations by which the journals are indicated, these abbreviations often requiring for their comprehension a "scientific use of the imagination." Many circumstances, national and individual, combine to produce confusion; the customs of divers countries vary greatly, and when English-speaking chemists adopt the abbreviations of French titles in use by German authorities, the result is not satisfactory from a bibliographical standpoint. The different tastes of some individuals, the thoughtlessness of others who seldom write a title twice in the same way, lead to the employment of many abbreviations for a single journal. Lest we may be accused of exaggeration we give a single example of this multiplicity of abbreviations; the voluminous and influential *Berichte der deutschen chemischen Gesellschaft zu Berlin* is referred to by writers in the following ways:—

B.
B. B.
Ber.
Ber. d. chem. Ges.
Ber. d. deutsch. chem. Gesellsch.
Ber. Berl. chem. Ges.
Berl. Ber.
Berichte.
D. C. Ges.
Deutsch. ch. Ges. Ber.

and doubtless in many more variations. Many other instances will occur to our readers who need no arguments to admit the desirability of a reasonable degree of uniformity in abbreviations of this kind.

When engaged in compiling "A Catalogue of Chemical Periodicals" (London, 1885) the writer contemplated adding thereto a list of abbreviations of the titles catalogued, but a sense of the inexpediency and futility of an assumption of authority caused an abandonment of the plan. Recently the subject has been broached by correspondents of the Committee on Indexing Chemical Literature, and a statement of the case seems advisable.

The existing lists of abbreviations for chemical periodicals, having a degree of completeness and possible authority, are not numerous. That monumental work of the Royal Society:—"A Catalogue of Scientific Papers (1800-63)," 8 vols., 4to, 1867-80, London, is the first to which one in search of reliable data would turn, but unfortunately this great work is bibliographically very unsatisfactory. The abbreviations of titles follow no definite plan, the first word abbreviated is sometimes the place of publication, sometimes the editor, and sometimes the first word of the title. We find such inversions as "Geol. Soc. Proc.," such redundant expressions as "*Gistl, Faunus*," and other evidences of a lack of system and of economy of space. The abbreviations in this catalogue cannot be adopted as standard.

Several chemical journals which furnish their readers with abstracts of contemporary literature have their own lists of abbreviations, but these are limited to journals now current, and the host of discontinued journals remain unprovided for. Nor are the abbreviations used by any means ideal: Thus we find in the valued *Jahresbericht* * * * *der Chemie*, several objectionable abbreviations, such as "Sill. Am. J." for the veteran American periodical which was so long associated with the name of Silliman; "Lond. R. Soc. Proc." in which the disorder is objectionable, an objection also applicable to the abbreviation, "*Russ. Zeitschr. Pharm.*"

In Mr. S. H. Scudder's Catalogue of Scientific Serials, we find an "Index to Titles," which is suggestive in many points although not prepared for use as abbreviations; nor does it give the abbreviations of Society transactions, the words Annals, Berichte, Journal, Bulletin, &c., being dropped for convenience. The care with which the abbreviated titles were prepared is, however, manifest in the skilful differentiation of expressions similar in orthography.

The most systematic and extended list of abbreviations of journal-titles appears to be that accompanying the Index-Catalogue of the Library of the Surgeon-General's Office, U.S.A. (Washington, 1880), and prepared by Drs. Billings and Fletcher. In this the authors clearly lay down the following principles for the construction of abbreviations on a uniform plan.

1. To follow the exact order of words of the title.
2. To make the abbreviations as brief as is consistent with clearness to those familiar with medical literature.
3. To follow strictly the orthographical usages of each language. This disposes of the question of capitalization.
4. To attain uniformity as far as possible.
5. The place of publication is generally added.

This work is intended for medical journals exclusively, but includes naturally a considerable number of chemical works. In the rules above quoted we find a basis for action, a definite method applicable to periodicals of every department of learning. While admiring the perspicuity of the contractions, the high degree of uniformity attained, and the consistency with which the rules are applied, we are, nevertheless, of the opinion that the abbreviations in this Index-Catalogue are in many cases unnecessarily long and cumbersome. This arises partly from retaining the initials of articles occurring in the title, partly from frequent addition of the place of publication even when it does not form part of the title, and largely from the praise-

worthy attempt to be consistent, especially in applying Rule 1. A single example taken from chemistry, will suffice to illustrate the occasion of our criticism. The well known journal popularly known as "*Berzelius' Jahresbericht*" has assigned to it the following abbreviation:—"*Jahresb. ii. d. Fortschr. d. phys. Wissensch. v. Berzelius, Tübing.*" This work is one of many having similarly unwieldy titles, and surely the abbreviation just given errs in like manner; chemists hastily noting the source of a reference cannot be expected to employ abbreviations of this character. Briefly, they are too consistent to be expedient.

Many journals, which have been conducted for a long series of years by a single editor of distinction, are known by that editor's name joined to the principal word of the title. While this is perhaps admissible in colloquial speech, abbreviations of these conventional titles are sometimes obscure and perplexing. Again, journals are sometimes quoted by prefixing the place of publication to the contracted titles, and this is another source of confusion. The propriety of avoiding these abbreviated, conventional titles in references is unquestionable, yet the most ardent adherent of bibliographical accuracy will hardly succeed in inducing chemists to forego speaking in such well established phrases as Silliman's Journal, Poggendorff's Annalen, Wagner's Jahresbericht, and Dingler's Journal, notwithstanding the fact that no persons of these names are longer connected with the respective periodicals. We do not believe perfect consistency between the spoken names and written abbreviations either necessary or desirable. On the other hand, the adoption of different names for different series of the same periodical, merely because a new editor has come into control, is a method of giving references which in our opinion cannot be too strongly condemned. In an exceedingly valuable work of reference, published last year, the author who adopts this unfortunate method designates a well known journal by no less than three sets of abbreviations, and is forced to admit that these are not always correctly applied. When the change of editorship is accompanied by renumbering of volumes the objection has less weight.

Many of the existing lists of abbreviations are designed to fill a special need in a particular work and are not suited to general use. This is true of the abbreviations in Dr. Carnelley's Melting and Boiling Point Tables, where restricted space demanded utmost condensation. In these tables the single letter "A" stands for Annalen der Chemie, "B" for the Berichte der deutschen chemischen Gesellschaft, "J" for Jahresbericht * * der Chemie, &c.

This suggests that the methods of designating periodicals may for convenience be classified in two groups, those in which a single letter is used, or at most two or three initials somewhat arbitrarily chosen, and second, those consisting of contractions of the words of the title; the first style may be called symbols, and the second contractions; both these classes occur in the abbreviations in general use.

The Problem in Chemical Bibliography which we have sketched in a desultory way is one which concerns not merely chemistry but the whole range of scientific literature. We think, however, that each branch of science should find its own interested expositors, and for this and other reasons we here limit the question to subjects properly coming before the Chemical Section.

The Problem has a two-fold aspect; first, in what way can a standard list of abbreviations of chemical periodicals be best prepared? and, secondly, How can such a standard list be presented to American chemists in a way to secure the widest acceptance? We propose that a co-operative effort be made to solve this problem, and suggest that it be referred to the Committee on Indexing Chemical Literature, reinforced by two bibliographers, to be added to its membership.

Trinity College, Hartford.
August, 1886.

Dr. Bolton's proposal for a Standard List of Abbreviations of Journal Titles was warmly endorsed by the Chemical Section, and the matter was referred to the Committee, with power to add to their number. This Committee is now constituted as follows:—Profs. H. Carrington Bolton, of Hartford; Albert R. Leeds, of Hoboken; F. W. Clarke, of Washington; A. A. Julien, of New York; John W. Langley, of Ann Arbor; Mr. S. H. Scudder, of Cambridge; Prof. Charles K. Wead, of Malone.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To COLONEL SIR FRANCIS BOLTON, *Water Examiner,*
Metropolis Water Act, 1871.

London, September 7th, 1886.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, the whole were found to be perfectly clear, bright, and well filtered.

The general character of the water supply of the month was unexceptionable. The mean proportion of organic carbon in the Thames-derived supply was 0.132 part, with a maximum of 0.157 part in 100,000 parts of the water, as against a mean of 0.146 part, and a maximum of 0.177 part in the preceding two months' supply.

Following up the series of bacteriological experiments with sterilised distilled water, described in our previous monthly report, we next made several series of more or less similar experiments with ordinary Thames-derived town-supply water. In one of these series of experiments the water was sterilised by repeated ebullitions, with removal by filtration of the earthy carbonates thrown down by the first ebullition. In another series the ebullitions were effected during the passage of a current of sterilised carbonic acid gas through the water, so as to maintain the earthy carbonates in solution; while in yet another series of experiments, made with a somewhat different object, the two modes of effecting the sterilisation were employed indifferently, the removal or retention of the earthy carbonates having been found without apparent influence on the bacteriological results. In each case addition of distilled water more than sufficient to compensate for loss by vaporisation, was made before sterilisation of the town-supply water, which was ultimately boiled down to just its original volume. After its sterilisation the water was allowed to become re-aërated by standing in cotton-plugged flasks before being subjected to experiment.

Seventeen experiments, all of them in duplicate, were

made with sterilised town-supply water, from which the earthy carbonates had been deposited by ebullition. The experiments were set going for the most part on different days, from March 19th to March 31st, inclusive. In each experiment a quantity of peptone fluid, loaded with an active sporeless growth of *Bacillus anthracis*, was added to the sterilised water in the proportion of about 1-150th of its bulk. To contaminate even a single day's supply of water to London, in the same degree, would require an addition thereto of at least a million gallons of bacillus-charged animal fluid; or an addition of at least half a million gallons of this same fluid to the eighty or so million gallons of the Thames-derived daily supply. The water, infected as above, was kept at about the temperature of the air of the room, which, in the course of different experiments, varied from 59° to 64° F. (15° to 18° C.). After different intervals of time tubes of sterilised culture-fluid were next sown with the infected water and subjected to incubation at 90° F. (32° C.). The general result of this series of experiments was as follows. The culture-fluid, when sown with the infected water, within three hours of its being infected, invariably developed on incubation an abundant characteristic growth of bacillus. On the other hand, the results afforded by sowing with the infected water, after it had been infected from four to seven hours, were very irregular—so much so that in some cases there was no development in the incubated culture fluid sown with a four hours' infected water, while in other cases there was development in the like culture fluid sown with a seven hours' infected water. Sowings after the lapse of more than seven hours had to be put off until the next morning, and were made habitually after an interval of eighteen hours from the original infection. In fifteen out of the seventeen duplicate experiments these sowings were found to be infertile; and as regards the two exceptional instances, in one of them the sowing with one of the two duplicate lots of water experimented on was infertile. Moreover, sowings made on the next following morning with the exceptionally behaving examples of infected water were in both instances infertile; showing that these waters, though retaining their power of setting up a growth of bacillus for an exceptionally long time, nevertheless lost their power within a couple of days.

Subsequent investigation showed that the extreme duration of infectivity in purposely infected water, extending in two experiments of this series to over eighteen hours, varied according to the proportion of nutrient animal fluid with which the water was contaminated. As already mentioned, the proportion of nutrient matter added to the river water made the subject of this series of experiments was extravagantly large. With a yet greater proportion there was observed to be a yet longer extreme period of infectivity; while conversely, with a lessened proportion there was observed to be a shorter period of infectivity, which, in the case of river water still contaminated with nutrient fluid to about one-fourth of the extent employed in the above series of experiments, was found not to exceed six hours. Particulars of a series of experiments establishing this result will be given in our next monthly report.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

The Composition of Forest Air.—E. Ebermayer.—The proportion of carbon dioxide in the air of woodlands is not sensibly smaller than that of the air of the open fields. The influence of a wood of 1 hectare in furnishing oxygen is neutralised by the respiration of four persons. The entire forest territory of Bavaria gives off yearly to the atmosphere 20 "milliard" kilos. of oxygen. —*Biedermann's Centralblatt für Agrik.-Chem.*, xv., pt. 5.

VERIFICATION OF THE CALCULATION OF
THE ATOMIC WEIGHTS OF M. STAS.

By J. D. VAN DER PLAATS.

(Concluded from p. 172.)

C. Molecular Weights of the Alkaline Chlorides and
Bromides.I HAVE calculated the molecular weights of these salts
according to their relation to silver, taking $\text{Ag} = 107.93$.

IX.	{ Independent value de- duced from KClO_3 . }	KCl	74.6143	74.5681	{ 74.6022 [74.5898] }
X.	"	KCl	74.6013	74.5991	74.6002
XI.	"	NaCl	58.5046	58.5011	58.5030
XII.	"	NH_4Cl	{ 53.5344 53.5338 }	53.5319	{ 53.5331 53.5329 }
XIII.	"	KBr	119.0975	119.0833	119.0884*
XIV.	"	NaBr	103.0083	103.0038	103.0061
XV.	"	NH_4Br	98.0347	98.0326	98.0340
XIX.	"	LiCl	42.4823	42.4777	42.4801

* According to experiment No. 9.

To control the average results more rigidly we calculate
as follows:—

$$\text{KBr} - \text{KCl} = 119.0884 - 74.6022 = 44.4862$$

$$\text{NaBr} - \text{NaCl} = 103.0061 - 58.5030 = 44.5031$$

$$\text{NH}_4\text{Br} - \text{NH}_4\text{Cl} = 98.0340 - 53.5330 = 44.5010$$

According to the at. wts. admitted, $\text{Br} - \text{Cl} = 44.499$

D. Atomic Weights of the Alkaline Metals.

We calculate these with the average results (C), ad-
mitting $\text{Cl} = 35.456$ and $\text{Br} = 79.955$.

$$\begin{aligned} \text{KCl} - \text{Cl} &= \begin{cases} 39.1442 \\ 39.1462 \end{cases} \\ \text{KBr} - \text{Br} &= 39.1334 \\ \text{NaCl} - \text{Cl} &= 23.0470 \\ \text{NaBr} - \text{Br} &= 23.0511 \\ \text{NH}_4\text{Cl} - \text{Cl} &= 18.0770 \\ \text{NH}_4\text{Br} - \text{Br} &= 18.0790 \\ \text{LiCl} - \text{Cl} &= 7.0241 \end{aligned}$$

The atomic weight of potassium, calculated from the
chloride, is more probable than that deduced from a single
estimation (No. 9) of the bromide.

From this there results:—

	Possible error.
$\text{K} = 39.144$ 0.01
$\text{Na} = 23.049$ 0.005
$\text{NH}_4 = 18.078$ 0.005
$\text{Li} = 7.024$ 0.01

E. Molecular Weights of Nitrates.

We accept $\text{KCl} = 74.6$; $\text{NaCl} = 58.503$; $\text{LiCl} = 42.48$;
 $\text{Ag} = 107.93$.

XVII.	KNO_3	101.1933	101.1864	101.1897
XVIII.	NaNO_3	85.1041	85.0925	85.0980
XX.	LiNO_3	69.0726	69.0675	69.0706
XVI.	AgNO_3 (dried)	169.9858	169.9853	169.9856
XVI.	AgNO_3 (melted)	169.9749	169.9676	169.9713

With $\text{NaCl} = 23.049 + 35.456 = 58.505$ we get for the
average value of $\text{NaNO}_3 = 85.1009$.

F. Atomic Weight of Nitrogen.

Admitting $\text{K} = 39.144$, $\text{Na} = 23.049$, $\text{Li} = 7.024$
 $\text{Ag} = 107.93$, we deduce the molecular weights of the
nitrates.We get at the same values by deducting the molecular
weight of a chloride from that of a corresponding nitrate.
The difference represents $\text{NO}_3 - \text{Cl}$, and is greater than
the atomic weight of nitrogen by $48 - 35.456 = 12.544$.In the year 1865, while submitting some results to cal-
culation under the law of probabilities, M. Stas found
 $\text{N} = 14.044$ with a probable error of 0.000718. The pro-
bability that the true value would be $\text{N} = 14.05$ was 0.00004,
and that $\text{N} = 14.055$ it would be 0.0... (twenty zeros) 02.
The last value seemed excessively improbable. But in 1882
M. Stas admits that $\text{N} = 14.055$ according to the synthesisof nitrate of silver dried at its melting-point, the relation
of the specific gravities of nitrogen and oxygen gases, and
according to the three last transformations of chloride of
sodium into nitrate.But the specific gravities of gases are not a reliable
means of calculating atomic weights exactly. M. Stas
himself says: * "The only means at arriving at a true
relation is to found the data on gravitation" (*Bulletin de
l'Académie Belgique*, 1880, vol. 1., p. 411). Besides,
Jolly (*Wiedemann's Annalen*, 1879, vol. vi., p. 529) has
fixed the relation of the specific gravities of oxygen and
nitrogen at 0° and 720 m.m. at about—

Maximum	..	16 : 14.0826
Minimum..	..	16 : 14.0782
Mean	16 : 14.0802

If the composition of nitrate of silver was definitely
fixed we should prefer it to all other means of calculating
the atomic weight of nitrogen. It is probable that the
transformations of chloride which have given the maxi-
mum of nitrate are the nearest to the truth. But so long
as the question, What is the normal composition of
nitrate of silver? is not answered, so long will the atomic
weight of nitrogen be uncertain.

I admit as correct:—

	Possible error.
$\text{N} = 14.05$ 0.01

This uncertainty is the more annoying as it deprives
us of a method of controlling the relation between oxygen
and hydrogen. In fact, as $\text{NH}_4 = 18.078$ and $\text{N} = 14.04$
to 14.06, $\text{H}_4 =$ from 4.038 to 4.018, and the relation—

$$\frac{\text{O}}{\text{H}} = 15.85 \text{ or } 15.93.$$

Even in giving full weight to the uncertainty which
exists about the atomic weights of silver, chlorine, and
bromine, it is impossible to admit that NH_4 is less than
18.065, and I conclude from this that $\frac{\text{O}}{\text{H}}$ is less than 16.0.†

* "La Science et l'Imagination."

† By the estimation of the water, which is produced by the oxida-
tion of a known volume of hydrogen (15 litres), I have recently found
this relation to be 15.94 to 15.96.

KNO_3	14.0493	14.0424	14.0457	M. Stas, β 288.
NaNO_3	14.0551	14.0435	{ 14.0490 14.0519 }	14.043
LiNO_3	14.0486	14.0435	14.0466	14.048
AgNO_3 (dried)	14.0558	14.0553	14.0556	14.046
AgNO_3 (melted)	14.0449	14.0376	14.0413	14.044 to 14.042

G. Atomic Weight of Lead.

Admitting $S=32.06$ and $N=14.05$ we deduce for lead:—

XXII.	$PbSO_4$	206.9411	206.8320	206.9028
XXI.	PbN_2O_6	207.0272	206.8816	{ 206.9550 [206.9417]

The last synthesis gives—

with $N=14.044..$	206.9355
and $N=14.055..$	206.9721

But the synthesis of the nitrate leaves grave doubts, that of the sulphate being far more delicate than all the others. I have, therefore, some hesitation in proposing:—

Possible error.

$$Pb=206.91 \dots \dots 0.05$$

In conclusion I give a table of the results of all my calculations:—

extract is then evaporated to dryness, and the nitric acid is determined in the aqueous solution of the residue.

In determining ammoniacal nitrogen the expulsion of the ammonia is effected by caustic magnesia. The use of potassa or soda is rejected, to obviate the decomposition of any cyanides present. To ensure the complete decomposition of ammonium-magnesium phosphate, if present, the sample is previously treated with an acid.

As indicator in titration litmus alone is to be used; phenolphthaleine is inadmissible.

Organic nitrogen is to be determined according to the Will-Varrentrapp method. When it is difficult to take a sample (leather, wool, &c.) a large portion is treated with sulphuric acid and an aliquot portion is submitted to combustion.

In mixed manures the ammoniacal nitrogen is determined by decomposition with caustic magnesia, and in

Atomic Weights, $O=16$.

	According to M. Stas.			According to my results.		
	1860. α 335.	1865. β 23.	1882. γ 64.	Atomic Weight.	Possible Error.	Logarithm.
Ag	107.943	107.930	107.930	107.930	0.01	2.0331422
Cl	35.46	35.457	—	35.456	0.005	1.5496897
Br	—	79.952	—	79.955	0.01	1.9028456
I	—	126.850	—	126.857	0.01	2.1033144
S	32.0742*	—	—	32.06	0.01	1.5059635
K	39.13	39.137	39.1425	39.144	0.01	1.5926652
Na	23.046†	23.043	23.0455	23.049	0.005	1.3626521
Li	—	7.022	—	7.024	0.01	0.8465845
N	14.041	14.044	14.0550	14.05	0.01	1.1476763
Pb	{ 206.906 (sulphate) 206.920 (nitrate)	{ — —	{ — —	206.91	0.05	2.3157815

* Calculated from the analysis of sulphate of iron, admitting $Ag=107.943$.

† M. Stas gave 23.05 (β 290) by mistake.

Molecular Weights.

Table.	Calculated direct from experiment. $Ag=107.93$.	Formulæ.	From the sum of admitted atomic weights. (ammonium excepted).	Logarithms.
D	18.077 to 18.079	NH_4	18.078	1.2571504
C X.	74.6022 to 74.6002	KCl	74.600	1.8727388
C XI.	58.5030	NaCl	58.505	1.7671930
C XIX.	42.4801	LiCl	42.480	1.6281845
C XII.	53.533	NH_4Cl	53.534	1.7286297
IV.	143.39095	AgCl	143.386	2.1565068
C XIII.	119.0884	KBr	119.099	2.0759081
C XIV.	103.0061	NaBr	103.004	2.0128541
C XV.	98.034	NH_4Br	98.033	1.9913723
VI.	187.8718	AgBr	187.885	2.2738921
VIII.	234.7885	AgI	234.787	2.3706740
E XVII.	101.1897	KNO_3	101.194	2.0051548
E XVIII.	85.0980	$NaNO_3$	85.099	1.9299245
E XX.	69.0707	$LiNO_3$	69.074	1.8393146
E XVI.	169.9856 to 169.9713	$AgNO_3$	169.980	2.2303978

REPORT OF THE COMMISSION OF FRENCH
AND BELGIAN CHEMISTS,
ON THE
METHODS OF EXAMINING MANURES.
(EXTRACT).

Determination of Nitrogen.

For nitrogen present as nitric acid the method of Schloësing is adopted. The purity of the nitric oxide gas evolved must always be tested by its complete absorption in an acid solution of ferrous sulphate: The determination is always effected in an aqueous extract.

In mixed manures containing organic matter, in which filtration is difficult, the sample is first treated with lime and then extracted with 50 per cent spirit. The alcoholic

the residue the organic nitrogen according to Will-Varrentrapp.

In manures containing nitric acid and ammonia, each kind of nitrogen is determined according to the method as laid down for it above.

In substances containing nitric acid and organic nitrogen the nitric acid is determined according to Schloësing, and the organic nitrogen according to Will-Varrentrapp, in a fresh portion from which the nitric acid has been expelled by treatment with ferrous chloride or oxalic acid.

Total nitrogen is determined on the principle of Dumas, by combustion with copper oxide. Ruffle's method can be applied only after the expulsion of the ammonia. Kjeldahl's method is repudiated, as in presence of nitrates chlorine may be liberated from the chlorides and decompose ammonia.

Determination of Potash.

In examining crude potassium chloride the platinum method is preferred; in mixed manures the method of Corenwinder. The sample must be ignited prior to analysis. The determination of potassa as perchlorate is too costly, on account of the large quantity of absolute alcohol required.

Corenwinder's Method. — The aqueous solution is strongly acidified with hydrochloric acid, and mixed with excess of platinum tetrachloride. The liquid is evaporated on the water-bath to a moist mass, and when cold digested in alcohol and ether. It is then placed on a filter, and washed with alcohol and ether until the filtrate is colourless. The potassium-platinum chloride remaining on the filter is dissolved in boiling water, when a yellowish residue is left undissolved. The solution is decomposed at a boil with solution of sodium formiate until colourless, and the precipitate of platinum is washed with hydrochloric acid, dried, weighed, and from its weight the potash is calculated.

Determination of Phosphoric Acid.

Total phosphoric acid is to be determined by dissolving the sample in hydrochloric acid and precipitating the phosphoric acid in an aliquot portion by means of magnesium citrate and ammonia. After twelve hours the precipitate is filtered, washed, dissolved in dilute nitric acid 1:10, sodium acetate added, and the liquid titrated with uranium nitrate.

The determination of soluble phosphoric acid is to be effected in an aqueous extract; reverted acid is to be dissolved by digesting the residue with ammonium citrate.—*Chemiker Zeitung.*

NOTICES OF BOOKS.

History of the Royal College of Surgeons in Ireland, and of the Irish Schools of Medicine; including numerous Biographical Sketches; also a Medical Bibliography. By Sir CHARLES A. CAMERON, P.R.C.S., Ireland. Dublin: Fannin & Co. London: Baillière, Tindall, and Cox. 1886. Royal 8vo.

THIS work, which has been written by the Professor of Chemistry to the Irish Royal College of Surgeons, will be read with great interest by all lovers of scientific history, comprising as it does in a complete manner an account of the foundation and rise of medical science and education in Ireland. It contains the biographies of several distinguished Irish chemists; for example, Sir Robert Kane, Professors Apjohn, Barker, Gregory, and Reynolds, and it gives much interesting information relative to scientific discoveries in Ireland, particularly to those made by Whitley Stokes (cousin of the present President of the Royal Society), McBride, and others. The book consists of about 750 pages, divided into twenty-one chapters. The opening chapter describes the progress of medical knowledge in Ireland from the earliest ages, and gives an account of medical works published in Ireland up to the year 1700. The second chapter details Irish medical biography in the eighteenth century. In Chapter 3 we find the history of the Barber-Surgeon's Guild in Dublin, incorporated in 1446, being by sixteen years the earliest incorporation of medicine in the United Kingdom. Chapter 4 gives a long account of medical education and institutions in Great Britain and Ireland prior to the nineteenth century. Then in eight chapters the history of the Irish College of Surgeons is given, two of them being devoted to an account of the college library and museum. The next chapter contains an account of the connection of the college with the Army and Navy Medical Departments, and is prefaced by a historical notice of British and Irish Army Surgeons from the time of McLiog, surgeon to King Brien Boru, who met the

fate of so many other Irish kings, by being killed in battle at Clondarf in 1014.

The lives of the seventy-three Presidents of the college are given in three bulky chapters, whilst the five remaining ones are devoted to an account of the medical schools of Ireland and the lecturers in them. Altogether nearly three hundred biographies are given, amongst which will be found the names of almost every distinguished Irish medical man of the present and former ages. The work may be regarded as a history, in some respects a full one, of Irish medicine and medical men. It contains numerous anecdotes, and abounds in quotations from curious old Irish works, describing medical men, surgeons, and apothecaries; it is adorned by numerous engravings and furnished with a copious index.

Proceedings of the Eighth Annual Meeting of the New York State Pharmaceutical Association, held in Rochester, January 8th, 9th, and 10th, 1886. Elmira, New York: Advertiser Association.

THIS report contains much interesting matter. From a paper contributed by Dr. R. G. Eccles it appears that salicylic acid is not a substance which can be indiscriminately used with safety. Hence we may fairly infer that its use to prevent fermentation in foods and beverages is open to very grave objections, since it may frequently thus find its way into the system of persons to whom it is likely to prove dangerous.

"Glucose syrup" seems to have given rise to considerable discussion. No one will, of course, contend that the natural sugar of the grape is unwholesome; but an artificial glucose may vary in quality according to the raw material used and the reagents employed. From evidence which has reached us it appears that the American glucose, made from maize-starch, is a wholesome product. Whether as much can be said in favour of the glucose manufactured on the European continent, from potatoes, is a very different question. Alcohol obtained by means of the fermentation of the potato is especially rich in the deleterious higher alcohols, such as the amylic. Hence it would seem that such glucose must be accompanied by undesirable by-products not found in the true grape-sugar.

The question of the sale of alcoholic liquors by pharmacists was considered at some length, and, whilst all the members present wished that they should not be degraded to the position of liquor-dealers, much diversity of opinion prevailed. In one district it appears that all pharmacists who made affidavit that they would not sell liquor except for strictly medicinal purposes are not required to take out a license.

The subject of the adulteration both of food and drugs engaged the attention of the Association. Two materials had been handed to Dr. Eccles, one used for adulterating pepper and the other for adulterating mustard. "These are from a large New York house, and all their business consists in sending them out for use as adulterants."

Of another substance, not distinctly named, but probably nux vomica, we read—"It is made into pills, and while the normal dose is three pills, a person could easily take from one to two hundred without any injury."

In a discussion upon a paper on the hypophosphites, read by T. D. McElhence, we find a remark on the comparative wages paid to manufacturing chemists in London and in America. It is said—"An Englishman receives more pay than an American. The idea that Americans receive more pay than Englishmen is fallacious." This statement will be received with surprise.

Newcastle-upon-Tyne Mining, Engineering, and Industrial Exhibition (International and Colonial). Royal Jubilee Year, 1887.

In spite of the strong doubts entertained in many quarters whether "international" exhibitions are calculated to be

in the least beneficial to a country placed under such circumstances as is the United Kingdom, the *furor* for these displays shows few symptoms of abatement. This, however, is a matter lying outside the sphere of the CHEMICAL NEWS.

The document before us gives a list, *in extenso*, of the vice-presidents, members of executive council, executive committees, and other officials. The divisions of the intended display are—Coal-mining and products; machinery; marine engineering and machinery, and naval architecture; civil, military, railway, and hydraulic engineering; building industries; chemical industries, including the three classes alkali, glass, and paints and oils; fisheries, agriculture, horticulture, and arboriculture, including manures; hygiene, arranged under the heads of warming and ventilating, gas-lighting and manufacture, and electric lighting; food; sundry industries and products, including tanning and paper-making; art in industries; and, lastly, science and education.

Reid's Patent Indexed Ready Reckoner, showing the value of 1 to 50,000 Articles at any given rate from $\frac{1}{16}$ of a Penny to a Pound, with Tables of Weights and Measures. London: Hamilton, Adams, and Co. Newcastle-on-Tyne: Sidney Reid.

THIS work, which has been checked by an experienced accountant, will effect a great saving of time in commercial establishments.

The tables of weights and measures cannot be considered as on a level with the age. There is no mention of the metric system, with which every person doing a foreign business requires to be familiar. Concerning Troy-weight we find the obsolete statement that it is used "in philosophical experiments." Such is not the case. Wherever weighing occurs in any scientific experiments the standards used are either the gramme or the grain, each with its multiples or sub-multiples; the troy pennyweight, ounce, &c., being entirely laid aside.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Justus Liebig's Annalen der Chemie,
Vol. ccxxxiv., Part 3.

Researches on Titanium.—(First Treatise).—Baron Otto von der Pfordten.—The author concludes from his experiments that: Pure sulphuretted hydrogen gas is obtained by removing oxygen with chromous chloride and drying with phosphorus pentoxide. Hydrogen gas obtained in the ordinary manner from zinc and acid contains no admixture of oxygen. For titanium and a number of other elements having a strong affinity for oxygen the sulphides are better obtained from the chlorides and sulphuretted hydrogen than by the action of carbon disulphide, which does not yield pure products. At low temperatures sulphuretted hydrogen reduces titanium tetrachloride, and forms at higher ones another compound, probably a sulpho-chloride. At a red heat there is formed pure crystalline titanium disulphide, into which the former products are converted. Titanium disulphide is oxidised by a current of carbonic acid free from oxygen. In a current of nitrogen or in a current of hydrogen at the temperature attainable in a glass tube, it is resolved into sesquisulphide. At the red heat of platinum it is reduced by hydrogen to monosulphide. The author compares and describes the sulphides just mentioned.

On China Bicolor.—O. Hesse.—The author concludes that Hodgkin's results, described in the *Pharmaceutical*

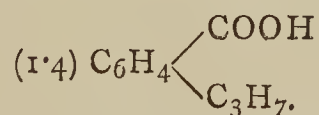
Journal, were due to the accidental admixture of a quantity of the bark of *Remijia pedunculata*.

Contributions to the Knowledge of the Azo- and Diazo-Compounds.—O. Wallach.—The author describes the conversion of nitrotoluidine into para-aceto-meta-toluyldiamine, para-acetamido-toluol-ortho-azo-dimethyl-aniline, para-amido-toluol-ortho-azo-dimethyl-aniline, toluol-ortho-azo-dimethyl-aniline para-azophenol, toluol-ortho-azo-dimethyl-aniline para-azo- β -naphthol, para-acetamido-toluol-ortho-azo-diethyl-aniline, ortho-aceto-meta-toluylen-diamine, ortho-acetamido-toluol-para-azo-dimethyl-aniline, ortho-amido-toluol-para-azo-dimethyl-aniline, acetamido-benzol-meta-azo-dimethyl-aniline, and amido-benzol-meta-azo-dimethyl-aniline.

On Cinchol.—O. Hesse.—The author shows the identity of this substance with Liebermann's cholestol or oxyquinoterpene.

Journal für Praktische Chemie.
New Series, Vol. xxxiv., Part 2.

Synthesis and Constitution of the Two Acids



—Richard Meyer.—The author discusses here the synthesis of cuminic acid, the preparation of isopropyl-bromide, the synthesis of cymol, the preparation of cuminic acid from synthetic cymol, and the synthesis of para-propyl-benzoic acid.

Part 3.

On Ortho-paradinitro-sulpho-benzolic Acid and its Derivatives.—C. Willgerodt and P. Mohr.—This acid is very hygroscopic and deliquescent. It forms long, transparent, pale yellow crystals, of the thickness of the thumb, and containing 3 mols. of crystalline water. The anhydrous acid is readily soluble in water, in lyes, and in alcohol, sparingly soluble in ether and glacial acetic acid, insoluble in benzol and boiling petroleum ether. If the acid is mixed with an excess of alkali it assumes at once, even in the cold, an intense dark yellow colour, which points to the abscission of the sulpho-group and the transformation of the sulphacid into a salt of *o*-dinitrophenol.

The Decomposition of the Vapour of Ethyl Ether by a Current of Induction Sparks.—M. von Klobukow.—The products of the decomposition are oxygen, carbon monoxide, hydrogen, CH_4 , and nitrogen. The author recognises in the extraordinary decomposing power of the arc, and of the current of induction sparks, the result of the united actions of thermic and electric energies, which energies occur simultaneously in especially favourable proportions in the above sources of force. By increasing one or other of these energies we are able to obtain the proportion necessary for a given decomposition. For each decomposition this proportion is naturally a constant which in a secondary degree may be influenced by other forms of energy, such as magnetism, light, &c. The state of a chemical compound exposed to the action of such a combination of forces may be likened to the "critical condition" of gases.

Promiscuous Notes.—Dr. J. Walter.—These notices comprise the introduction of H_2N by means of sodium amide, the application of phosphoric anhydride as a desiccating agent, the author recommending that it should be compressed into a compact mass, the flocculent state being very inconvenient; and on the occurrence of acridine in the last product obtained during the distillation of crude diphenylamine.

The Electrolysis of Normal Capronic Acid by Alternating Currents.—E. Drechsel.—The author's experiments prove that in electrolysis with alternating

currents there are obtained quite different products from those yielded by currents of a constant direction.

On the Radicle Paracyanogen and its Compounds with the Halogens.—Peter Klason.—Paracyanogen contains at least six carbons in its molecule, and bears the same relation to the paracyanides as does free cyanogen to the cyanogen compounds.

On β -Naphtho-acridine.—J. H. Reed.—The author obtained this base, hitherto unknown, in long straw-coloured needles, which melt at 216° .

Bulletin de l'Association des Elèves de M. Fremy.
2nd Series, No. 6. April, 1886.

Review of Certain Qualitative Analytical Procedures founded upon Micro-Chemical Reactions.—L. Bourgeois.—This paper will be inserted at some length.

On Different Simple Methods for recognising Silver, Nickel, and Tin deposited in Thin Layers on Metallic Objects.—L. Loriton.—The first method consists in scorching the object in the oxidising flame of a Bunsen burner, and observing the series of colouration-phenomena shown by the surface under the progressive action of heat. This series is constant, and sharply characteristic of each of the three kinds of surfaces considered. The second process, still more simple, consists in plunging the object for some minutes into a strong, boiling solution of sodium chloride. In the former method we observe successively, in case of a surface coated with nickel, a yellowish grey colour, distinct violet reflections, a blue colour with bright black reflections, and, lastly, a uniform grey tint with green reflections. A surface coated with tin shows a dirty yellow-grey colouration; slight violet reflections, rapidly passing off; a grey tint with a dotted surface, and a wrinkled surface with distinct yellow spots. A silvered surface shows at first no change appreciable by the naked eye; small violet points; an abrupt change to a uniform grey with white points and a yellowish grey wrinkled surface. With the solution of sodium chloride the results obtained are—with nickel a reddish violet colouration at the end of ten minutes; with tin, a dull grey colouration scarcely to be distinguished; and with silver, nothing. Dilute ammonium hydrosulphate, slightly heated, blackens silver, strips tin, and has no action upon nickel.

Apparatus of M. Schaufler, chiefly intended for the Determination of Nitrogen in Ammoniacal Salts and of Carbonic Acid in the Carbonates.—This apparatus cannot be usefully described without the accompanying figure.

New Model of an Incineration Furnace.—V. Wiesnegg.—The same remark applies to this device.

Antidotes for the Poisonous Chemical Products commonly used in Industry.—For phenol, creosote, tincture of iodine, and phosphorus, use white of egg well beaten up in water and a spoonful of mustard in warm water. If sulphuric, nitric, or hydrochloric acid, or aqua regia has been swallowed, take chalk stirred up in the smallest possible quantity of water. For chromic acid, the chromates, chrome colours, and antimonial preparations, such as tartar emetic, use white of egg in abundance, and a mustard emetic except in case of tartar emetic. Tea of marine herbs (?) is also recommended. For ammonia, potash, soda, alkaline silicates, and hydrosulphates, employ vinegar, followed up with oil or milk. For hydrocyanic acid, the cyanides and sulpho-cyanides, oil of bitter almonds, and nitro-benzol, pour cold water upon the head and spine, apply mustard to the soles of the feet and the region of the heart, and keep the patient awake. For ether, petroleum, benzol, fruit essences, or strong alcohol, use a strong mustard emetic with plenty of warm water, cold water and fresh air externally, and keep the patient awake. For compounds of lead and

barium use the mustard emetic, and give Epsom or Glauber's salts. For arsenic and its compounds, the mustard emetic, dialysed iron with magnesia, and then oil, milk, or mucilaginous liquids. For oxalic acid and soluble oxalates use chalk, lime-water, and castor-oil. For silver nitrate take common salt dissolved in water, and finally the mustard emetic. For gaseous nitrogen oxides use small quantities of acetic acid as strong as it can be taken.

Carbon Disulphide Burner.—M. Ckiandi.—The apparatus here described and figured serves to generate sulphurous acid for disinfecting rooms, ships, wearing apparel, &c.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. 4th Série. Vol. i., No. 7, July, 1886.

Production of Azo-Colours.—The dyes obtained by the action of the phenols upon thion-aniline appear to be industrially useless, whilst those extracted from thio-paratoluidine are very valuable. We dissolve, *e.g.*, 40 kilos. thio-paratoluidine in 500 litres of water with 120 kilos. of ordinary hydrochloric acid. After letting the solution stand for three hours the liquid is poured into a mixture of 145 kilos. soda lye at 33° B., and a solution of 130 kilos. sodium- β -naphthol-bisulphate in 1000 litres of water cooled down to 5° . The colour obtained is salted out and purified by repeated solution. Industrial dyes are also prepared by the action of diazothio-paratoluol upon the sulph-acids of the α and β naphthols and of the α and β naphthylamines. The colours obtained from the naphthol sulph-acids furnish tones ranging from brown to reddish blue, whilst those yielded by the naphthylamine sulph-acids give tones ranging from a yellow to a red-brown. The colours produced by the naphthol sulphoacids β are remarkable for the slowness with which they are deposited upon the fibre and their fastness on washing.—*Dingler's Journal*.

MISCELLANEOUS.

Fuels: their Uses and Economy.—A free introductory lecture to this course, to be held during the coming Winter at King's College, London, will be given by Mr. W. G. McMillan, F.C.S., at 7 p.m., on Monday, October 11th, the subject being "Heating Methods and Fuels of the Past and Present."

Congo-Red as a Reagent for Free Acid.—Prof. Hugo Schulze.—The author has utilised Congo red to decide the question whether the lower animals produce free acid internally. It dissolves readily in water and has the advantage of not disturbing the vital functions of the lower animals. He found, *e.g.*, that Rotatoria are stained distinctly blue in their digestive region, whilst their other parts remain white if a drop of a strongly coloured solution of Congo red is allowed to flow under the covering glass; the existence of free acid is thus demonstrated, though its nature can scarcely be determined.—*Central-Blatt für Med. Wissenschaft und Chemiker Zeitung*.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Utilisation of Oak Shavings.—I have a considerable quantity of fine oak shavings. Can any of your correspondents suggest a method of utilising the same?—O. P. Q.

TO CORRESPONDENTS.

Homo de Scotia.—We do not understand the question.

THE CHEMICAL NEWS.

VOL. LIV. No. 1403.

WATER OF CRYSTALLISATION IN SOLUTION.*

By W. W. J. NICOL, M.A., D.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham.

WHEN a hydrated solid salt is dissolved in water it is generally considered that the molecules of water of crystallisation remain as an integral part of the salt and distinct from the remainder of the water present in the solution.

In the course of experiments on the molecular volumes of dissolved salts I was led to a conclusion entirely opposed to the generally received view, inasmuch as I found that the whole of the water in a solution possessed the same molecular volume, and that it was impossible to distinguish between water of crystallisation and solvent water. I was thus led to examine more closely the evidence in support of the commonly accepted view, and the following paper consists of an attempt to summarise the existing evidence on this point and to ascertain the bearing of this evidence.

There are in all three sources from which we can hope to obtain information sufficiently exact and complete to enable us to approach an answer to this problem. These are—

1. Thermo-chemical evidence, comprising data as to heats of solution, of hydration, of neutralisation, &c.
2. Volume-chemical evidence (to employ the English form of the term used by Ostwald), consisting of measurements of the molecular volumes of salt solutions, and the change of volume on double decomposition, &c.
3. Evidence derivable from the colour of dissolved salts. This is of necessity limited in its range, but is of very considerable importance at first sight.

The evidence obtainable from a careful study of thermo-chemical results is the most complete, if not the most conclusive, at our disposal, and is generally regarded as proving the existence of water of crystallisation in solutions,—at least of those salts which, when dehydrated, evolve heat on solution in water. The form of the argument is as follows:—

When a crystallised hydrated salt is dissolved in water heat is absorbed, while, on the contrary, when the same salt is dehydrated and then dissolved in water, heat is evolved. It is therefore clear that hydration occurs on solution. But the argument is in this form incomplete and fallacious; for it ignores the fact that the sum of the thermal changes in the above actions expresses the heat of hydration of the solid salt by means of liquid water, and that no account is taken of what may occur after the solid hydrate is formed. The argument is completed by adding that, if the solid hydrate formed above is split up again on solution, then the heat of hydration disappears from the scene, and the heat of solution is that of the dehydrated salt: but this is positive, while the heat of solution of a salt which does not crystallise with water is negative; there is thus a constant difference in the behaviour of the two classes of salts. To what can this be due, if not to hydration?

Before attempting to answer this question let us consider whether we have any grounds for assuming, as is

usually done, that the heat of hydration of a solid salt is any measure of the affinity existing between that salt and water. At first sight this would certainly appear to be the case, but on further reflection it is found that a great many other circumstances have to be taken into consideration. Thus there is the thermal change due to the passage of the water from the liquid to the solid state: this has to be deducted from the heat of hydration, and is a very large amount, in some cases exceeding the whole heat of hydration, so that the heat of hydration of cadmium chloride, minus the heat of change of state of $2\text{H}_2\text{O}$, is a minus quantity. This is, it is true, an extreme case, but the others are similar; there is not the slightest trace of a connection to be observed between the heat of hydration and the number of water molecules in the hydrate. Salts with an exceedingly small hydration heat per molecule of water unite with 10 or 24 molecules; others, with six times as high a value, unite only with 2 or 6 molecules of water. Surely nothing more need be said to prove that water of crystallisation and heat of hydration are not connected in the very simple way that is generally assumed.

Our knowledge of thermo-chemistry is not I believe sufficiently advanced to enable us to solve this problem; still I think it is possible to trace out the probable explanation of this apparently anomalous behaviour of salts. In nearly every chemical action, and certainly in the hydration of salts, there are involved not only chemical but also physical changes. Thermo-chemistry of necessity makes, in very many cases, no distinction between these two, as they appear to be inseparably connected, and no means are at hand to enable us to assign to each part of the change its correct thermal value. So far all is right, but what is unjustifiable is the custom of assigning chemical significance to a thermal change which has its origin in physical as well as chemical changes; and this is, I believe, what is done with the heat of hydration. When a dehydrated salt unites with water to form the solid hydrate, it is not sufficient to deduct from the thermal change the value of the change of state of the water, and then to assume that the remainder is the measure of the chemical affinity existing between the salt and the water, for that leads to an absurd result in the case of cadmium chloride, and, as I have shown, to no result with other salts from which it is possible to trace out a connection between water of crystallisation and corrected heat of hydration. There can, then, be no doubt that the process of hydration involves other changes, probably physical, in addition to those already taken account of.

It is to the probable nature of these that I wish to direct attention. The heat of fusion of three salts has been examined,—chromate, phosphate, and thiosulphate of sodium,—and has been found to be respectively 12,300 cal., 23,900 cal., and 9,400 cal. Now these numbers comprise not only the liquefaction of the water, but also that of the salt. In each case, the change of state of the water being deducted, we have $-2,100$ c., $+6,600$ c. and $+2,200$ c., and for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ the figures are 8,900 c. and $+0,273$ cal.

There is thus no relationship to be observed; in one case the liquefaction of the salt is attended by an absorption of heat, as was to be expected, but, on the other hand, it produces the most varied amounts of heat in three cases out of four. The formation of a solid hydrate is then of a very complicated nature, and one in which the chemical affinity between salt and water probably plays but a secondary part, the physical changes undergone by both salt and water accounting in many cases for nearly the whole of the thermal change,—in some cases for more than all.

Passing now to the act of solution of a solid anhydrous salt, such as NaCl . This is in nearly every case an endothermic process, and at first sight it is difficult to understand how it is possible for it to dissolve at all, for spontaneous chemical changes are always exothermic,

* Discussion on the "Nature of Solution," British Association, Birmingham Meeting, Section B.

while solution is endothermic and yet spontaneous. When, however, we regard it not as a chemical action, but as a physical one, partially if not entirely as a change of state, then the anomaly disappears, for we find that spontaneous physical changes may be endo- or exothermic, as the case may be. Thus evaporation is always endothermic, but the conversion of sulphur from the prismatic to the octahedral form is exothermic, and many other cases will occur to my readers; the explanation apparently being that purely physical changes, when endothermic, are seldom if ever attended by degradation of energy, but exothermic changes are, and are not reversible in the same way as endothermic changes.

It is, I think, the case that the purely physical change from the solid to the liquid state is always endothermic; there is also no doubt that there exists an attraction (physical or chemical) between the molecules of salt and the molecules of water which produces contraction, and that this is exothermic. The thermal change attending solution will therefore depend for its sign on the relative values of these + and - changes. Now it seems probable, as will be seen later, that the + value above is a constant for most salts in dilute solution, and this is supported by the fact that the effect of a molecule of salt in diminishing the vapour-pressure of water is very nearly constant, as is shown not only by my results, but also by those of Wüllner and Tammann. Now the + side of the thermal account being a constant, it follows that the total depends solely on the magnitude of the - side; that is, on the thermal change attending the passage of the salt from the solid to the dissolved state: this is an entirely physical process, and consists in the separation of the molecules from one another. If we assume for a moment that this is large in the case of anhydrous salts, and small in that of the dehydrated ones, then all is perfectly clear. Is there any ground for such an assumption? There is indeed little doubt that hydrated salts are more soluble than corresponding anhydrous salts, — *e.g.*, Na_2SO_4 than K_2SO_4 , BaCl_2 than $\text{Ba}(\text{NO}_3)_2$, and other instances; but a comparison of this kind is of necessity limited, for there are but a few cases in which it can be made. At present I believe it is not possible to prove that this assumption is a correct one, but it is highly probable, for, as I have shown, the thermal change on hydration is but small in many cases when that due to the solidification of the water is deducted, and in no case is it possible to connect it with the number of molecules of water of crystallisation. On the other hand, when we consider not the heat of hydration, but that of solution of the anhydrous or dehydrated salts, then we find a host of relations existing between the various salts, as pointed out by Thomsen. Thus it is probable that the act of solution is a simpler and less complex process than that of the formation of the solid hydrate. Now if the endo- or exo-thermic character of the solution of a salt be conditioned, as pointed out above, by the relative magnitudes of the force tending to produce solution and the work necessary for the separation of the salt molecules from one another, it follows that the thermal change, on dilution of the solutions thus formed, should have the same sign as that attending solution, but that there should *not* be a strict line of demarcation between the two classes; certain members of each class should behave as members of the other class on dilution. Thus it is found that nearly all salts which are endothermic on solution are also so on dilution, and *vice versa*, but that there are a few exceptions which, so to speak, form the connecting-link between the two classes. These exceptions are $\text{Zn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ exothermic on solution, and so also on dilution with a small amount of water, but endothermic in very dilute solution. Four other salts out of the thirty-five examined by Thomsen show what he regards as anomalous behaviour, but in reality occupy the intermediate position spoken of above.

Turning now to the evidence obtainable from the thermal change on neutralisation of an acid with various

bases, we find that it is conclusive against the existence of water of crystallisation in solution. I shall at present consider only the neutralisation results directly obtained, as there can be no uncertainty about them. The figures given by Thomsen are contained in the following Table, and they show most clearly that for these bases the heat of neutralisation with sulphuric acid is a constant, and with hydrochloric acid and nitric acid it is another constant, differing from the former by -3,520 cal.

TABLE I.

Base.	H_2SO_4 .	H_2Cl_2 .	$\text{H}_2\text{N}_2\text{O}_6$.
$\text{Li}_2(\text{OH})_2$	31,290	27,700	—
$\text{Na}_2(\text{OH})_4$	31,380	27,490	27,360
$\text{K}_2(\text{OH})_4$	31,290	27,500	27,540
$\text{Tl}_2(\text{OH})_2$	31,130	(27,520)	27,380
$\text{Ba}(\text{OH})_2$	Insoluble.	27,780	28,260
$\text{Sr}(\text{OH})_2$	30,710	27,630	—
$\text{Ca}(\text{OH})_2$	31,140	27,900	—
Means	31,160	27,650	27,630

It is on this constancy of difference between the figures for H_2SO_4 and H_2Cl_2 , and the exact agreement of the figures for H_2Cl_2 and $\text{H}_2\text{N}_2\text{O}_6$, that the following argument is based. When sulphuric acid neutralises each of these bases the result is first the separation of 2 molecules of water, then the union of the metal and the salt radical to form a salt. So far the changes are common to all the salts formed, and there is no cause to wonder at the constancy of the thermal change, but if water of crystallisation exists in solution each of the salts thus formed combines with water: Li_2SO_4 with 1 molecule, and evolves 1,200 cal.; Na_2SO_4 with $10\text{H}_2\text{O}$ + 4,820 cal.; K_2SO_4 with none; Tl_2SO_4 with none; so also with SrSO_4 ; while CaSO_4 unites with $2\text{H}_2\text{O}$, evolving -3,300 cal. I have assumed in the above that Thomsen is correct in stating that the bases and acid themselves exist in solution without water of crystallisation; if such is not admitted the argument is only stronger.

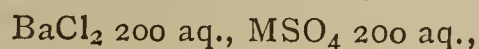
Pass now to the chlorides and nitrates. The salts of potassium and sodium are anhydrous (so with thallium), but barium chloride unites with $2\text{H}_2\text{O}$, evolving 4,120 cal.; $\text{Ba}(\text{NO}_3)_2$ is anhydrous; SrCl_2 and CaCl_2 are both hexhydrated, evolving respectively 9,000 cal. and 13,000 cal. There is then the greatest possible diversity to be observed in the water of crystallisation, and yet the thermal results are constants. Will anyone ask us to believe that this constancy is attained by the adjustment of the heat of neutralisation proper? Surely that would be contrary to the probabilities of the case, which is enormously against that explanation, and even this last loophole of escape is closed by a comparison of the figures for the sulphates, chlorides, and nitrates of potassium and sodium. It is likewise useless to contend that a solution of a salt formed by neutralisation differs from one produced directly: all evidence is to the contrary. The thermal results for organic bases which form stable salts lead to the same conclusion; but enough has been said to justify the conclusion of Thomsen, that "different substances when in aqueous solution are in an analogous condition," and "I regard the state of solution as a condition in which substances may be compared with reference to their thermal relationships with the same success as is done in the gaseous state with regard to their other physical properties"; and this, I may add, would be impossible were water of crystallisation present.

Again, the division of a base between two acids—the "avidität" of Thomsen and the "affinität" of Ostwald—throws some further light on this subject; for no matter how this is ascertained, whether by the thermal changes or the volume changes, or by the rate of inversion of sugar or of etherification, the result is in all cases the same; and it must be noted that the first two methods may include water of crystallisation, but the last two cannot. Surely it is almost certain that nowhere, when

dealing with solutions, are the reactions complicated by water of crystallisation.

Having shown above that the thermal results are free from water of crystallisation, it remains to be seen whether water of constitution has any effect on them; for experiments on the volumes of salt solutions have led me to the conclusion that it exists in solution (see below). I believe that thermo-chemical results do show a trace of the presence of water of constitution. Unfortunately, however, none of the bases whose salts are concerned in this question are soluble in water; thus we cannot attack the question directly.

Thomsen has examined the reaction—

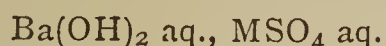


and his results show that when—

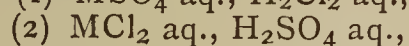
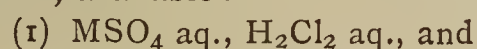
$$\text{M} = \text{K}_2 \text{ or } \text{Na}_2, \text{ R} = -5,260 \text{ cal.},$$

$$\text{M} = \text{Mg, \&c.}, \text{ R} = -5,620 \text{ cal.},$$

showing a difference of 360 cal., the results of the reaction.



cannot be considered, for they are complicated by the heat of formation of the solid hydrates Mg(OH)_2 , &c., which are unknown. The results of partial decomposition are, however, available:—



and are as follows:—

$$\text{M} = \text{K}_2 \text{ or } \text{Na}_2 \left\{ \begin{array}{l} (1) -3.276 \\ (2) +0.554 \end{array} \right\} = -3.825$$

$$\text{M} = \text{Mg, \&c.} \left\{ \begin{array}{l} (1) -2.455 \\ (2) +1.106 \end{array} \right\} = -3.561,$$

and the difference here is $\frac{3}{2}$ (264 cal.), the mean of the two differences obtained from the methods of double and partial decompositions being 380 cal.,—a small amount, it is true, still exceeding the limits of experimental error according to Thomsen, for he himself says “an alteration of the relative avidität of the two acids with the nature of the base is therefore recognisable.” “It appears, however, that the *avidität* varies slightly within each group of bases; for the alkalies it is 0.5–0.57, for the magnesium series it is 0.7–0.81, and these two groups therefore are distinct from each other.” Ostwald has found the same by the comparison of the volume changes, but neither attempt to account for this difference, and Thomsen actually in the latter part of his work entirely overlooks the difference he has found and thus emphasized, and makes the difference in the heat of neutralisation of H_2SO_4 and H_2Cl_2 a constant for all the bases.

I wish, however, to lay stress on this point: even if this difference between the two classes of bases be due to the water of constitution, the value 380 cal. is small compared to the thermal value of hydration of the salt with 1 molecule of water, being in many cases but a tenth of what was to be expected. It is this fact that led me to regard the heat of hydration as due in most part to physical rather than to chemical changes.

We have now to consider the volume-chemical results. If dilute solutions, not more than 1 equivalent of salt to 100 molecules of water, be compared, it is found that their molecular volumes when compared in series—that is, the salts of two metals with various acids, and *vice versa*—exhibit constant differences; thus the salts of potassium with various acids, compared with those of sodium with the same acids, have a constant difference of 10.4 units. This has been shown to hold good for twenty-nine inorganic and organic acids. Now this constant difference in volume obtains in spite of the utmost diversity in the water of crystallisation in the solid state, which varies from 0 up to 12 H_2O . This proves that all the water present in the solutions has the same volume, which could not be the case were water of crystallisation present. The same holds good for all the salts I have yet compared, with the single exception of those which contain water of

constitution. Here it is found that the difference in volume between the chlorides of the magnesian series and the corresponding sulphates is markedly less than that observable between other chlorides and sulphates. This leaves us the alternative of assuming either that the water of constitution makes the difference or that for some unexplained reason these salts alone form an exception. Surely there can be no hesitation as to which is the more reasonable view. I may add here that, by water of constitution, I do not wish to commit myself to any theory as to its nature. There can be no doubt that in the magnesium sulphates *one* of the molecules of water is retained by the salt at a higher temperature than the others, if the experiment be quickly performed, though it is equally probable that complete dehydration may result from prolonged heating at a low temperature, just as ice, however cold, ultimately completely evaporates. The above difference in the behaviour of solutions of the salts of the magnesian series from others, though only observed by me, is completely supported by the results of Ostwald and others, when these are calculated in the form of molecular volumes.

Finally, we have the colour changes of solutions as throwing light on the question of hydration. A great deal of importance—far too much indeed—has been attached to these as proving the existence of hydrates in solution. The argument would indeed have great weight were it contended that cobalt chloride, for example, existed in the same state in solution as in the solid state after drying at 150° C., but such a contention is manifestly absurd. All that I maintain is that a solution is truly homogeneous, that the whole of the water present in a dilute solution stands in the same relation to the salt, and that condition can be satisfied without assuming that the salt is entirely separated from the water. In fact the vapour-pressures of salt solutions show clearly that the presence of a single molecule of salt is sufficient to disturb the equilibrium of a relatively infinite mass of water molecules. The thermal and volume changes have shown that water of crystallisation is indistinguishable from solvent water, and I believe I am justified in maintaining that there is nothing in the colour of salt solutions incompatible with this view.

It must not be overlooked that the whole of this paper has reference solely to dilute solutions. When a solution is saturated the conditions are entirely different, and there can be little doubt that at the crystallising point *some* of the salt-molecules have water of crystallisation attached to them.

ON THE ARSENATES OF CALCIUM.

By CHARLES L. BLOXAM.

IN analysing the arsenate of calcium and ammonium an attempt was made to determine the ammonium in the form of $2\text{NH}_4\text{Cl.PtCl}_4$ by dissolving in HCl, evaporating with excess of PtCl_4 , and treating with alcohol, but the platinum salt was lighter yellow than usual, and when ignited left a residue weighing half as much again as the Pt calculated. On boiling the residual platinum with strong aqua regia it left a white granular powder, quite insoluble in acids, and appearing under an inch objective in fine white, opaque, prismatic crystals.

Fused with Na_2CO_3 the substance gave CaCO_3 , corresponding to 29.6 per cent of Ca, and $\text{MgNH}_4\text{AsO}_4 \cdot \frac{1}{2} \text{ aq.}$, corresponding to 36.26 per cent of As.

The formula $\text{Ca}_3(\text{AsO}_4)_2$ requires 30.15 per cent of Ca and 37.69 per cent of arsenic.

The insoluble substance appears, therefore, to be the tricalcic diarsenate corresponding to the bone phosphate.

I then endeavoured to obtain the salt by synthesis, employing Iceland spar as the source of calcium and pure As_2O_3 for the arsenic, these being dissolved in excess of

nitric acid to convert all the arsenic into arsenic acid, evaporated to dryness, and strongly ignited to decompose and expel the excess of arsenic acid.

(1). 6.03 grains CaCO_3 and 3.96 grains As_2O_3 ($\text{Ca}_3:\text{As}_2$) gave a residue weighing 7.98 grains. $\text{Ca}_3(\text{AsO}_4)_2$ requires 7.9998, but this was not crystalline, and was soluble in HCl .

(2). 6 grains CaCO_3 and 4 grains As_2O_3 ($\text{Ca}_3:\text{As}_2\cdot 02$) gave a residue weighing 8.01 grains, which lost no more on repeated ignition over a gas blowpipe. The residue was strongly alkaline, and dissolved almost entirely in HCl .

Hence it appears that 3 molecules of CaO are capable of retaining 1 molecule of As_2O_5 at a bright red heat.

Experiments were next made with gradually increasing proportions of arsenic, 6 grains of CaCO_3 being taken for each experiment, and the ignition conducted over the blowpipe till the weight was nearly constant.

	1.	2.	3.	4.	5.
As_2O_3 in grains	4.50	5.00	5.50	6.00	10.00
Ignited residue	8.46	9.00	9.46	9.86	11.52
Calculated $\text{CaO} + \text{As}_2\text{O}_5$	8.59	9.17	9.75	10.33	14.98

These numbers show that the amount of arsenic which remains unexpelled at a bright red heat increases rapidly with the proportion of As_2O_3 employed. This is explained by the behaviour of As_2O_3 when oxidised by HNO_3 , evaporated to dryness, and ignited, when a considerable quantity of a vitreous residue remains, which diminishes in weight very slowly at a red heat, and contains both As_2O_3 and As_2O_5 , being probably the same substance which is produced by heating As_2O_3 in Cl .

On boiling these residues with strong HCl it was found that in those cases in which an excess of As_2O_3 had been employed a considerable quantity of a granular powder remained undissolved. This appeared, under the microscope, to consist of groups of prisms, white and opaque, but not nearly so large as those previously obtained.

When 3 grains of CaCO_3 and 10 grains As_2O_3 were treated with excess of HNO_3 , and strongly ignited, the residue did not give up any Ca to boiling HCl , the whole of that metal being left in the granular powder.

To determine the composition of this insoluble body it was fused with sodium carbonate, and treated as described above.

Substance.	Found.		Calculated $\text{Ca}(\text{AsO}_3)_2$.		
	Ca.	As.	Ca.	As.	Ca : As.
3.53	0.472	1.78	0.493	1.85	1 : 2
3.74	0.532	1.88	0.523	1.96	1 : 1.9
3.57	0.476	1.80	0.499	1.87	1 : 2
1.61	0.224	0.86	0.225	0.84	1 : 2.05

The insoluble substance, therefore, appears to be the calcium metarsenate, $\text{Ca}(\text{AsO}_3)_2$.

The three arsenates of calcium correspond to the phosphates.

Tricalcic diarsenate, or Orthoarsenate, $\text{Ca}_3(\text{AsO}_4)_2$.

Pyroarsenate, $\text{Ca}_2\text{As}_2\text{O}_7$.

Metarsenate, $\text{Ca}(\text{AsO}_3)_2$.

The analysis of the pyroarsenate was given in the CHEMICAL NEWS (vol. liv., p. 168).

I have endeavoured to obtain the crystallised orthoarsenate again by the method referred to at the commencement, but have only obtained the metarsenate.

POSTSCRIPT TO "ARSENATE OF CALCIUM AND AMMONIUM" (vol. liv., p. 168).

Some light has been thrown upon the reason for the difference of opinion with respect to the amount of water in the salt, by the result of an experiment in which two samples of the salt which had been freely exposed to air for four warm days in August till the loss of weight was insignificant, were allowed to remain exposed to the air, and weighed at intervals of about twenty-four hours,

until, instead of losing, they began to gain slightly as the atmospheric temperature fell. This did not happen until after thirty-six days, during which period six minima of loss were observed, the first occurring when the formula of the salt was $\text{CaNH}_4\text{AsO}_4 \cdot 7\text{H}_2\text{O}$, and the last when the loss corresponded to a final residue of $\text{CaNH}_4\text{AsO}_4 \cdot \text{H}_2\text{O}$, the intermediate points of minimum loss in equal periods corresponding approximately to the loss of successive molecules of water. Hence, if an observer analysed the salt when the second minimum loss had been arrived at, he would pronounce it to have the composition—



I regret that, not at all anticipating the result, I did not keep so careful a record of the daily hygrometric, thermometric, and barometric conditions during the thirty-six days as would enable me to plot trustworthy curves; and I look forward to another period of leisure and fairly equable temperature to extend the experiment to some other hydrated salts in order to ascertain whether any general law can be deduced as to the periods of minimum loss.

In the precipitation of calcium from waters as ammonioarsenate, it will be noticed that it is preferable to add the arsenic acid (or ammonium arsenate) before adding the ammonia, which may, in some cases, give an immediate precipitate of CaCO_3 or $\text{Mg}(\text{HO})_2$.

King's College, London, October 4, 1886.

ON SOME CHEMICAL PROPERTIES AND CONSTANTS OF SODIUM BICHROMATE.

By ARTHUR STANLEY.

CONSIDERING the growing commercial importance of sodium bichromate, which has of late years been sold on a large scale as a substitute for potassium bichromate, a more thorough knowledge of its chemical and physical properties has become desirable. At the request of Dr. Knecht I therefore undertook a series of experiments with a view of supplying some information on the chemical and physical properties of this important compound. In the first edition of Gmelin Kraut's "Handbuch der Chemie" a brief notice is found of sodium bichromate, which is said to exist in six-sided prisms, but no other data are given.

The crystals, $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O}$, were examined by Siewert, *Fahresberichte*, 1862, and *Haller Zeitschrift*, xix., 11. With the exception of what is given in the patent literature and in one or two publications describing its manufacture, very little has hitherto been published on sodium bichromate in technological or scientific handbooks or journals.

The sodium bichromate used in these experiments was one of White's (Glasgow) manufacture, which was in the condition of an almost anhydrous crystalline mass, containing a very small percentage of chromic oxide, as seen by the following analysis:—

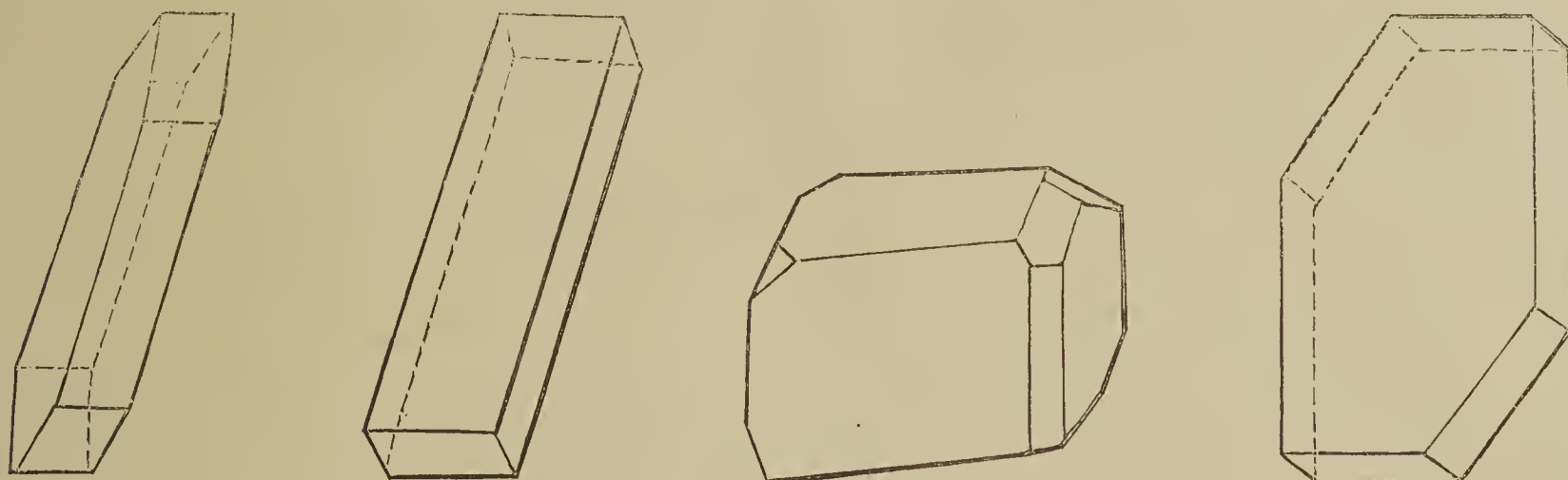
Sodium bichromate ..	98.360
Water	1.523
Chromic oxide	0.135
	100.018

Another sample of White's crystallised commercial products, after drying, yielded the following results on analysis:—

- (1). 1.0660 grm. of bichromate, after boiling with strong HCl and precipitating with ammonia, gave 0.6190 grm. $\text{Cr}_2\text{O}_3 = 0.8130$ grm. $\text{CrO}_3 = 76.2$ per cent CrO_3 . Theoretical, 76.3 per cent.
- (2). 1.0890 grms. of sodium bichromate, after same treatment, gave 0.6330 grm. Cr_2O_3 , corresponding to 99.97 per cent of $\text{Na}_2\text{Cr}_2\text{O}_7$.

Sodium bichromate crystallises in prisms and plates belonging to the triclinic system. When crystallised from a hot solution it assumes the form of long prismatic needles, but when allowed to deposit from a cold solution, as in one slowly evaporating at the ordinary temperature of the air, it crystallises in short pyramid-capped prisms.

The following are the most general forms of the crystals which I observed:—



These crystals are of a deep red colour, transparent and deliquescent, and have the formula $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O}$. The first molecule of water is given off on heating below 75° , while all the water is given off below 100° , leaving the anhydrous salt as a light brown mass.

The crystals of $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O}$ have a sp. gr. of 2.5246 at 13° .

When the crystals of the hydrated salt are dissolved in water a considerable reduction of temperature occurs, while if the anhydrous bichromate be treated with water a rise in temperature is produced, thus proving that in the latter case, the salt, before solution, chemically combines with water to form a hydrate.

Water at the ordinary temperature dissolves about its own weight of sodium bichromate. One hundred parts of the saturated solution contain:—

At—	0°	15°	30°	80°	100°	139°
$\text{Na}_2\text{Cr}_2\text{O}_7$	107.2	109.2	116.6	142.8	162.8	209.7

The saturated solution boils at 139° , at which temperature it contains more than 200 parts of the salt. It is insoluble in ether, but slightly soluble in absolute alcohol, becoming more so the greater the quantity of water present; for example, 100 c.c. of strong methylated alcohol, of sp. gr. 0.8225 dissolved 2.80 grm. of sodium bichromate at 17° .

The specific gravities of the aqueous solutions of sodium bichromate are the following, taking as the strength the percentage of the salt in a given quantity of solution:— (See Table, next column).

About half the above figures are the results of direct experiment, the other half being obtained by interpolation.

Sodium bichromate has an acid reaction, and a sharp, bitter, cooling, metallic taste.

Sodium bichromate, whether in the anhydrous or hydrated condition, is very hygroscopic. In order to give an idea of the relative absorptive power for moisture of the anhydrous bichromate, I performed the following experiment: Taking coarsely powdered anhydrous bichromate and ordinary calcined, granulated calcium chloride in equal quantities (viz. 5.1679 grm.), and exposing to the atmosphere, it was found that sodium bichromate possessed about one-third the absorptive power of calcium chloride. After exposing for four hours the increase in weight in each case was:—

CaCl_2 .	$\text{Na}_2\text{Cr}_2\text{O}_7$.
0.3489	0.1159

After forty-eight hours the increase due to absorption was:—

5.1399	1.7930
--------------	--------

Thus it is seen that after forty-eight hours the calcium

chloride absorbed about its own weight of water, while in the same time and under the same circumstances sodium bichromate absorbed approximately a little over one-third its own weight.

The anhydrous bichromate fuses at 320° , forming a transparent dark red liquid, which, on cooling, crystallises in the same forms as the hydrated salt deposited from the aqueous solution.

Percentage of $\text{Na}_2\text{Cr}_2\text{O}_7$ in solution.			Sp. gr.
1 per cent	1.007
2	1.014
3	1.021
4	1.028
5	1.035
6	1.042
7	1.049
8	1.057
9	1.064
10	1.071
11	1.078
12	1.085
13	1.092
14	1.099
15	1.105
16	1.113
17	1.120
18	1.127
19	1.134
20	1.141
21	1.147
22	1.153
23	1.159
24	1.165
25	1.171
26	1.178
27	1.185
28	1.193
29	1.201
30	1.208
31	1.216
32	1.224
33	1.231
34	1.238
35	1.245
36	1.252
37	1.259
38	1.266
39	1.273
40	1.280
41	1.287
42	1.294
43	1.300
44	1.307
45	1.313
46	1.319
47	1.325
48	1.330
49	1.336
50	1.343

Sodium bichromate decomposes at a temperature slightly above its fusing-point (320°). At about 400° it begins to give off oxygen, while at a temperature just below dull red heat the evolution of oxygen becomes almost violent, the salt decomposing into normal sodium chromate, chromic oxide, and oxygen.

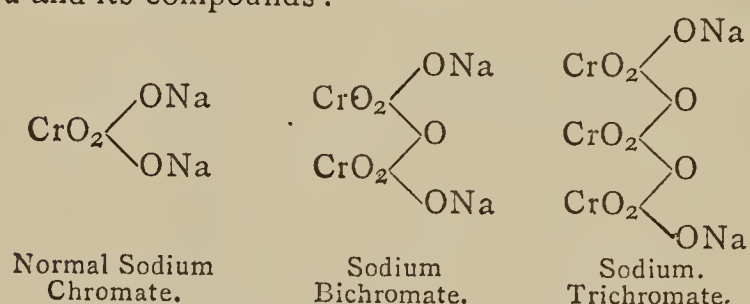


Amongst the products of decomposition a small quantity of free alkali was found, produced, no doubt, by a slight decomposition of the chromate.

If sodium bichromate be dissolved in warm aqueous chromium trioxide, and the solution allowed to cool, crystals of a dark red colour are deposited. These yielded, on analysis, the formula $\text{Na}_2\text{Cr}_3\text{O}_{10}$, and were, therefore, sodium trichromate.

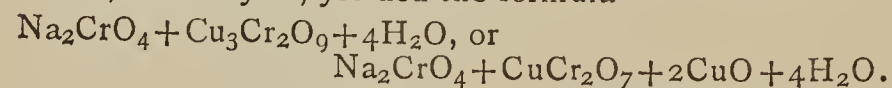
Calc. for $\text{Na}_2\text{Cr}_3\text{O}_{10}$.. Cr = 43.09 p.c. Found 43.14 p.c.

This compound may be represented graphically by the following constitutional formula, the chromates and their derivatives being represented as containing the dyad radical, chromyl, CrO_2 , analogous to the dyad radical sulphuryl, SO_2 , whose existence is assumed in sulphuric acid and its compounds:—



The crystals of sodium trichromate are very soluble in water, and deliquescent.

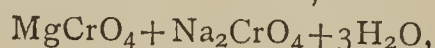
By the action of sodium dichromate on cupric hydroxide, which has been freshly precipitated, I obtained a substance which, on analysis, yielded the formula—



	Theory.	Found.
Sodium ..	6.84 per cent	6.89 per cent.
Chromium ..	23.21 ..	23.03 ..
Copper ..	28.35 ..	28.62 ..
Water ..	10.73 ..	10.84 ..

It is thus a compound of sodium chromate with a basic copper dichromate, $\text{CuCr}_2\text{O}_7 + 2\text{CuO}$. This substance occurs as a brown powder, which consists of microscopic crystals. It is almost insoluble in water, and slightly soluble in alcohol. On heating, the four molecules of water are given off below 200° , leaving the anhydrous substance as a dark brown mass, which latter, on heating to a higher temperature, partially decomposes, becoming black, owing to separation of cupric oxide.

When a solution of sodium bichromate, which has been neutralised with magnesia, is evaporated, the double salt, magnesium-sodium chromate,—



crystallises cut in yellow four-sided prisms and plates. It is soluble in water and alcohol, but insoluble in ether. All the water of crystallisation is given off below 200° , leaving the anhydrous compound as a dark reddish brown powder. At red-heat it fuses and partially decomposes.

Sodium dichromate has an acid reaction, and by caustic soda or the carbonate is converted to the normal sodium chromate, but by heating with metallic sodium it is reduced to chromic oxide. It is a powerful poison, like the potassium salt, probably on account of its oxidising properties. Sodium bichromate also acts like the potassium salt in its action on organic matter. If a film of organic matter be saturated with a solution of sodium bichromate, on exposure to light it becomes of a dark colour, which is caused by a reduction to chromic oxide occurring. This property of the bichromates is applied

in the arts in the autotype, and similar photographic printing processes.

The commercial salt is in some cases almost chemically pure; in others it is purposely made impure, owing to the fact that the purer it is the more hygroscopic it becomes. The fused varieties always contain a small percentage of chromic oxide produced by decomposition at the temperature of fusion.

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ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

1. Introduction.

It cannot be denied that the number of micro-chemical indications, of which we can avail ourselves in the study of minerals, to recognise certain constituents, is much less than those which serve to indicate the elementary substances of animal and vegetable tissues; and that the application of these last is much more extensive than that of the chemical reactions employed in divining the nature or composition of any mineral specimen.

It is evident that we cannot find the cause of this difference in the fact that the advantage of the micro-chemical analysis would be less when studying a mineral substance than when examining the nature of an animal or vegetable tissue. Indeed, those who have been engaged in the microscopic examination of minerals will agree that if it were possible to show, by micro-chemical means, the presence of potassium and sodium, and to estimate approximately the proportion of the constituents of feldspar with the same facility and precision that can be obtained in finding and estimating starch by means of iodine, or cellulose with iodine and sulphuric acid, there would result a great gain to petrography.

For some time past it has been found necessary to extend and improve the methods of microscopic examination in the determination of the component parts of rocks. Mr. Zirkel made his first researches by means of ordinary light; a year later he made use of polarised light, and some years after that, in his researches on the basaltic rocks, he often had recourse to hydrochloric acid to enable him to distinguish labradorite from oligoclase, and magnesite from titaniferous iron. Since then hydrochloric acid has become the usual reagent for microscopists. However, it has latterly lost somewhat of its prestige, inasmuch as we became too exacting, and did not take sufficient account of its temperature and concentration, nor the duration of the reaction; and also by not making blank experiments to control the results.

Generally speaking, however, we make use of it on account of its decomposing and dissolving action; but it is only occasionally that we pay attention to some of the products of decomposition, such as carbonic acid as a sign of the presence of calcite, sodic chloride produced by the decomposition of nepheline, gelatinous silicic acid as an absorbent of the colouring matters, so that we can more easily recognise the easily decomposable silicates, like olivine, chlorite, &c.

Among the micro-chemical reagents which have lately become known we might mention the reagent brought out by Fresenius (ammonic molybdate dissolved in nitric acid), which was employed by Streng, in his research on apatite in rocks from various sources; the colouration by sulphur vapour of several mineral species belonging to the group of haüynite and its allies, according to the method followed by Knop; and the colouration of the different varieties of opal by the solution of magenta.

While the application of chemical reactions made only slow progress, the improvement of optical methods which

could serve in the study of minerals was attracting considerable attention.

We borrowed from the zoological and botanical microscopes the use of plates of gypsum and quartz, to increase the effect of double refraction, for rotating optical axes, and for distinguishing between positive and negative double refraction.

Soon the researches of M. Tschermak (1869) gave an impetus to the microscopic study of dichroism in minerals, at first by means of M. Haidinger's di-chroscopic lens, and afterwards by means of two Nicol prisms, and at last we owed to the researches of M. Descloiseaux* on the optical constants of felspar, the application of M. Kobell's stauroscope to microscopic work. Then M. Rosenbusch rendered essential service to the science in giving a more convenient form to the apparatus which was used for observations of this character (1876), and by publishing his Micrographical Manual, which contributed largely to the spread of the microscopic examination of minerals.

Mechanicians and opticians then came to our assistance by constructing and perfecting machines for cutting and slicing minerals, so that the preparation of thin and transparent plates of mineral substances became much less laborious, and we were enabled to make sections in any direction without trouble. At the same time microscopes and all their auxiliaries were improved. It is only just to mention the workshops of Fuess at Berlin, and Seibert Bros. at Wetzlar, as being those which gave the impulse in this direction.

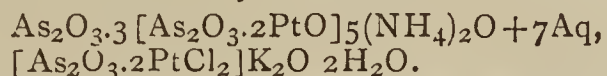
(To be continued.)

FURTHER RESEARCHES ON COMPLEX INORGANIC ACIDS.†

By Dr. WOLCOTT GIBBS.

You will doubtless remember the very interesting and curious results obtained many years since by Schützenberger by the action of phosphoric pentachloride upon spongy platinum. We have simply $\text{Pt} + \text{PCl}_5 = \text{PtCl}_2 \cdot \text{PCl}_3$, the compound by the action of water giving the corresponding acid $\text{PtCl}_2 \cdot \text{P}(\text{OH})_3$. A second and analogous compound chloride has the formula $\text{PtCl}_2 \cdot 2\text{PCl}_3$, and this yields the acid $\text{P}_2 \cdot \text{PtCl}_2 \cdot (\text{OH})_6$. A third acid has the formula $\text{P}_2 \cdot \text{PtCl}_2 \cdot (\text{OH})_5$, and a fourth is represented by $\text{P}_2\text{O}_2 \cdot \text{PtCl} \cdot (\text{OH})_3$. These compounds have attracted very little attention, perhaps on account of the neglect and contempt into which inorganic chemistry has fallen of late years. Schützenberger does not appear to have attempted to generalise his results. I have endeavoured to show, in a paper read before the National Academy of Science, that in Schützenberger's acids platinous chloride simply replaces an atom of oxygen, and that, by appropriate methods we ought to be able to perform the inverse substitution and obtain three new acids of phosphorus which would have respectively the formulæ $\text{P}_2\text{O}(\text{OH})_6$, $\text{P}_2\text{O}(\text{OH})_5$ or perhaps $\text{P}_4\text{O}_2(\text{OH})_{12}$, and $\text{P}_4\text{O}_7(\text{OH})_6$, since $2\text{PtCl}''' = 3\text{O}$. Of course the first acid mentioned above, $\text{P} \cdot \text{PtCl}_2 \cdot (\text{OH})_3$, is, on this view, ortho-phosphoric acid, in which PtCl_2 replaces one atom of oxygen. I have now succeeded in generalising these results in what seems to me an interesting manner. In the first place I have discovered compound acids analogous to chlor-platin-ortho-phosphoric acid, which contains respectively palladium, iridium, ruthenium, and osmium in place of platinum. Want of material has prevented me from experimenting with rhodium also, but it can hardly be doubted that it forms similar compounds. In the next place I find that platinous chloride may be replaced by platinous oxide or bromide, and the same appears to be

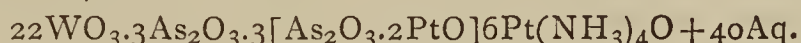
true for other metals of the platinum group. A still further generalisation consists in replacing phosphorus by arsenic and antimony, which is easily effected. It is to be expected that vanadium will yield similar compounds, but here again want of material has prevented the actual experiment up to the present time. The following formulæ, which are, I believe, to be depended on, will serve to illustrate my results—



As I have written it, the first compound might be called an arsenoso-oxyplatin-arsenate, and the second a chlorplatin-arsenate. When these compounds are digested or boiled with acid tungstates and molybdates, higher complex acids are obtained, which I am now studying. One tungsten compound appears to have the formula—



Another, the formula—



A beautiful pale green molybdenum compound has the formula—



All these compounds contain the oxide of platino-ditetramine, $\text{Pt}(\text{NH}_3)_4\text{O}$, as a base. The formulæ given, however, are only preliminary, and may hereafter prove reducible to simpler expressions. The salts were obtained by digesting or boiling the green salt of Magnus, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 + \text{PtCl}_2$, with arsenoso-tungstates and arsenoso-molybdates. Analogous series appear to be formed when arsenoso-phospho-tungstates and arsenoso-phospho-molybdates are digested or boiled with platinous chloride or with the tetramine salt. Now, replace platinum by other metals of the same group, and arsenic by antimony or phosphorus, perhaps also by vanadium, and you will have some idea of the extent of the new field of work in which I am now labouring as fast as my limited means and resources will permit.

THE ACTION OF REAGENTS ON COBRA-POISON.

By C. J. H. WARDEN, Surgeon, H M.'s Bengal Staff,
Professor of Chemistry, Calcutta Medical College.

Preliminary Note—Action of Heat.

THE experimental inquiry, detailed in the following communication, has been undertaken at the suggestion of Professor Koch,* of Berlin, with the object of systematically ascertaining the action of reagents on cobra-venom. I am well aware that researches of a similar nature have engaged the attention of many workers, and it is, therefore, with hesitation that I venture to undertake the investigation of a subject which has hitherto proved so practically unfruitful. Numerous antidotes have been suggested, but one and all have failed when employed on the human subject, and this, no doubt, arises from the fact that conclusions have been hastily arrived at, rather than carefully and patiently worked out. On the other hand, any accurate information regarding the action of reagents on snake-poison—be the facts discovered ever so small or apparently trifling—is a step in advance, and one towards the solution of that most important problem, the discovery of a reliable mode of treating cases of snake-bite.

In investigations regarding the action of drugs of a complex nature, it frequently occurs that the physiological action of the drug, considered as a whole, differs from its

* Several papers in the *Comptes Rendus* and the *Annales de Chimie et de Physique*, 1875 and 1876.

† From *American Chemical Journal*, Vol. VIII., No. 4.

* The experiments described in this note were performed in the Chemical Laboratory, Kaiserl. *Deutschen Reichs-Gesundheits Amt*, Berlin. I would take this opportunity of thanking Dr. Koch for his valuable advice in the conduct of my experiments, and Dr. Sell for permitting me to work in his laboratory.

isolated constituents. Thus, while opium is narcotic, thebaia, one of its constituents, is purely excitant, and in doses of one grain causes tetanic spasms (Farquharson). The experiments of Blyth, S. Weir Mitchell, and others, appear to indicate that snake-poison is a mixture of several toxic agents. According to Weir Mitchell the poison can be separated by dialysis into at least three proteid constituents. One, dialysable and resembling a peptone—"venom peptone" and apparently a hastener of putrefactive change, and a convulsive agent, but with little power to prevent coagulation of blood, and varying in different snakes. A second—"venom-globulin," a more deadly poison, acting powerfully on the blood and capillaries, so as to cause enormous local hæmorrhages at the point where the poison is injected. It was destroyed at 100° C. in all the venoms studied. The third proteid—"venom-albumin," resembles serum-albumin.

A research, therefore, of the nature I have undertaken includes experiments with the poison as a whole, and *secondly*, the action of reagents on its several principles. I propose dealing first with the venom considered as a whole, reserving until afterwards a consideration of its chemical composition, together with the action of reagents on its constituents.

In order to ascertain the influence of a reagent on the toxic power of snake venom, it is essential that the dose administered, admixed with the reagent, should be accurately the same as that employed in the control experiment, and *secondly*, that the quantity of venom should be the minimum dose which, with certainty, causes death. To administer an overwhelming dose mixed with the reagent and to expect any other than a fatal result appears to be futile, for even in the case of that small class of poisons for which we have antidotes the exhibition of a very large dose renders the operation of the antidote inutile.

The first question, therefore, which I attempted to solve, was the minimum fatal dose requisite for the class of animal selected for the experiments. This having been determined, the sample of venom was standardised. It need hardly be observed that in dealing with a toxic agent of such potency as cobra-venom, and one in which the line of demarcation between a fatal and non-fatal dose is so small, that this is a most important point.

In the experiments detailed in this note I have employed the dried venom, and it is perhaps preferable to the fresh poison, because, though the former may be somewhat less active, yet it is comparatively stable, and definite in composition, and a sample of one or two grms., after having been standardised, suffices for a large series of experiments. On the other hand, the fresh venom cannot be kept for any length of time without undergoing decomposition, the products of different snakes vary in toxic power, and hence to obtain comparable results, a number of standardising experiments are requisite. According to Wall—"Indian Snake-Poison"—specimens taken from several cobras and mixed, gave a specific gravity of 1058. On evaporation the fresh venom yields from 25 to 50 per cent of solid residue.

The cobra-poison used in this series of experiments was obtained from Prof. Koch, who had received it from Dr. V. Richards, of Assam. It consisted of two specimens, in the form of small, dry, transparent, yellowish fragments, one somewhat paler in colour than the other, but both having much the appearance of coarsely-pounded gum-arabic. In cold water—with the exception of a few small white flakes—the venom was readily soluble, yielding a very faintly acid solution, which frothed strongly on agitation, even in highly diluted solutions. Snake-venom, which has been dried by exposure to air, is usually considered anhydrous, or as only containing traces of moisture, but, as the following determinations indicate, a considerable percentage of moisture may be present. One of the specimens given me by Prof. Koch lost 16.26 per cent of water in the course of sixty-five days by being kept over concentrated sulphuric acid; a second

sample obtained from Prof. Pedler, of Calcutta, lost under similar treatment 15.43 per cent in thirty days.

In all my experiments, unless stated to the contrary, white or piebald China mice were employed. The necessary dose of the poison, &c., was always injected under the skin of the back by a small hypodermic syringe, of one cubic-centimetre capacity, graduated into ten parts, the graduations being marked on the piston rod.

Experiments to ascertain the minimum fatal dose for mice.—0.01 gm. of cobra-poison containing 83.74 per cent of anhydrous venom was carefully weighed, and dissolved in 10 c.c. of distilled water at 15° C.; 1 c.c. of the solution, therefore, equalled 0.001 gm. or 0.00083 gm. of the anhydrous poison.

Exp. 1.—Three mice injected—

(a) With 0.1 c.c. equal to 0.0001 gm. poison. Death in 36 minutes.

(b) With 0.3 c.c. equal to 0.0003 gm. poison. Death in 44 minutes.

(c) With 0.4 c.c. equal to 0.0004 gm. poison. Death in 33 minutes.

Mouse (a) weighed 14 grms. Ratio of poison to body weight, 1 to 140,000. In the case of mouse (b) part of the injection escaped.

Exp. 2.—As the solution used in the first experiment was evidently too concentrated, and as it was difficult to accurately inject more than 1 c.c., the solution was diluted with distilled water in the proportion of 1 to 9. One c.c. of the diluted solution was therefore equal to 0.0001 gm. of the poison. Three mice injected with the diluted solution:—

(a) With 0.1 c.c., equal to 0.00001 gm. Not fatal.

(b) With 0.2 c.c., equal to 0.00002 gm. Death in 1 hour and 50 minutes.

(c) With 0.4 c.c., equal to 0.00004 gm. Death in 58 minutes.

Exp. 3.—As a control experiment a fresh solution was prepared by dissolving 0.01 gm. in 100 c.c. of distilled water, and the solution filtered. Four mice injected—

(a) With 0.1 c.c., equal to 0.00001 gm. Not fatal.

(b) With 0.1 c.c., equal to 0.00001 gm. Not fatal.

(c) With 0.2 c.c., equal to 0.00002 gm. Death in 1 hour and 17 minutes.

(d) With 0.2 c.c., equal to 0.00002 gm. Lived over 3 hours.

Ratio of poison to body weight (c) 1 to 6,140,000 (d) 1 to 6,810,000.

In the case of (d) mouse part of the injection escaped, so that it received more than 0.1 c.c., but less than 0.2 c.c. Though life was prolonged for over three hours, the symptoms were most marked. Shortly after the injection the animal became restless; the breathing then became hurried, and accompanied every now and then by a squeak. Ultimately it fell on its side, and the respirations became gradually slower. There were no convulsive movements.

In the following table the results of the foregoing experiments are given in terms of anhydrous venom:—

(a) 0.000083 gm. Proved fatal in 36 minutes.

(b) 0.00025 gm. Proved fatal in 44 minutes.

(c) 0.00035 gm. Proved fatal in 38 minutes.

(d) 0.000355 gm. Proved fatal in 58 minutes.

(e) 0.000016 gm. Proved fatal in 1 hour and 50 minutes.

(f) 0.000016 gm. Proved fatal in 1 hour and 17 minutes.

(g) 0.000016 gm. Lived over 3 hours.

(h) 0.000008 gm. Not fatal.

(i) 0.000008 gm. Not fatal.

(j) 0.000008 gm. Not fatal.

Dealing thus with quantities of the anhydrous venom varying between 0.000016 and 0.000008 of a gramme, we have a series of six results which indicate that while the first-mentioned amount is a non-fatal dose, double the quantity is certainly fatal. With the indication afforded by Exp. 3 (d) we are justified in assuming that for the

particular sample of poison employed the minimum fatal dose of anhydrous venom for a China mouse is more than 0.000008 and less than 0.000016 of a gramme.

(To be continued).

NOTICES OF BOOKS.

Descriptive List of Experiments on the Fundamental Principles of Chemistry. By J. PARSONS COOKE. Cambridge: Harvard University. 1882.

THE Introduction to this pamphlet contains some good sound advice to students of chemistry, in which we note several rules which were laid down by W. R. Nichols and L. M. Norton in a pamphlet entitled "Laboratory Experiments in General Chemistry." These rules impress strongly on the student or operator the necessity of taking full and careful notes of all experiments *at the time*.

The first part of the pamphlet is devoted to a description of the properties and character of the different elements, with full directions for determining them: for example, under "Sulphur," we find—"The student should be given a roll of brimstone, and asked to study and describe its distinguishing properties, including colour, hardness, tenacity, specific gravity, fusibility, volatility, colour of vapour, and solubility in ordinary solvents." This method of making students thoroughly acquainted with the various chemicals they will have to deal with is undoubtedly better than the method which has been adopted of late years, of giving only a superficial knowledge, which can be quickly picked up, but alas! easily forgotten.

The second part is headed "General Principles," and the third treats of molecules and atoms. The definition here given of an atom of hydrogen is "the smallest mass of matter recognised by Science."

Part IV. is devoted to symbols and nomenclature; Part V. to molecular structure; and Part VI. to thermal relations, such as the heat of solution, precipitation, or chemical action.

This pamphlet promises to be exceedingly useful to beginners, and is evidently meant to teach and not to cram.

Analysis Tables for Chemical Students. By R. L. TAYLOR, F.C.S., F.I.C., Teacher of Chemistry and Physics in the Central Higher Grade Board School, Manchester. London: Sampson Low, Marston, and Co.

THESE tables are in their object essentially examinational. Both the title-page and preface inform us in substance that they are principally "for the use of students who are working for the advanced stage of the Science and Art Department examinations in practical inorganic chemistry and both the elementary and advanced stages of practical organic chemistry."

We have here doubtless the reason why so many of the metals, including, *e.g.*, the two platinum groups, are omitted, and why silicic and manganic acids do not figure among the list of inorganic acids.

The instructions in practical organic chemistry are limited to tests for the recognition of nine organic acids, including the salicylic, but excluding the tannic and gallic! For this curious selection Mr. Taylor cannot, indeed, be held in any way responsible. Like other science teachers he must, to a great extent, shape his course according to the winds blowing from South Kensington.

The reactions given are all, as far as we have been able to perceive, accurate; but the omissions and limitations which we have pointed out must greatly interfere with its usefulness to students not working on the lines of the Department. To take a single instance: in the table for testing for acids we are told that on adding hydrochloric acid to a substance and heating, the evolution of chlorine

"indicates a chlorate or a chromate." True, but it may also indicate a permanganate. Thus these tables are trustworthy only if the student knows that no substance is present save those which will be submitted to him at the Departmental Examination.

Laboratory Calculations and Specific Gravity Tables. By JOHN S. ADRIANCE, A.B., F.C.S. New York: John Wiley and Sons.

WE have here an exceedingly useful selection of tables, which will certainly, as the author hopes, save both the student and the analyst much tedious calculation.

The table of atomic weights shows the values as recalculated by Prof. F. W. Clarke, and includes such of the rarer metals as have been satisfactorily determined. Next follows a table of conversion-factors, commonly used in analysis.

There is a table of the absorption of carbonic acid in 5 c.c. of hydrochloric acid, at 1.125 sp. gr., for evolutions of between 1 and 100 c.c. There follow next tables of the weight of 1 c.c. of carbonic acid at different temperatures and pressures; of the absorption of nitrogen gas in hypochlorite solution; weight of 1 c.c. nitrogen for variations of temperature and pressure; table for converting nitrogen into ammonia; tensions of aqueous vapour for temperatures from -2° to $+110^{\circ}$; molecular weights, and weights of 1 litre of gases; and Beaumé's hydrometer scale for liquids heavier and lighter than water. Here we must speak guardedly; for although this scale is perfectly arbitrary, and exists in two, if not three, discrepant versions, and though the indications of the instrument cannot be translated into direct specific gravity by any simple calculation, yet were we to state the conviction that Beaumé ought to be discarded in favour of Twaddle we should perhaps find ourselves involved in a prolonged controversy.

Next follow the tables of Fownes and Gay-Lussac, giving the proportion of actual alcohol in 100 parts of spirits of different specific gravities. There are then factors for determining quantity of pure sugar by Ventze's and Duboscq's saccharometer; tables showing the percentages of the most important acids in aqueous acids of given specific gravities; similar tables for ammonia, soda, common salt, potash, calcium, barium, magnesium, aluminium, ammonium, copper and stannic chloride solutions, specific gravities, and percentages for solutions of a number of salts often met with in manufacturing operations; comparisons of thermometer scales from 100° down to -34.4° ; comparative table of barometer indications in inches and millimetres; comparison of air and mercurial thermometers; conversion of column of water into column of mercury; and tables of weights and measures. Here we meet with an apparent discrepancy. A pint is said (p. 69) to be equal 0.567636 litre, whilst on the next page it is said to contain only 0.473148 litre. Possibly the last-mentioned figures may refer to the old "wine-measure," which, we believe, is still current in the United States.

Concerning the value of this book in the laboratory no two opinions can prevail.

Universal Pharmacopœia. (Universal Pharmakopöe). A Comparative Conspectus of the Pharmacopœias at present valid in Europe and North America. By Dr. BRUNO HIRSCH. Vol I. Leipzig: Günther. London: Williams and Norgate.

DR. HIRSCH has evidently expended a great amount of time and labour in the compilation of the work before us, and is entitled to the gratitude of pharmacists and medical practitioners. His object is to pave the way for a universal pharmacopœia to be recognised among all civilised nations. He hopes that the collocation which he is carrying out

will render it easier in the future to pick out the best features from every national pharmacopœia, and unite them into a totality preferable to anything which has yet appeared. This, he is fully aware, will be no easy matter; the crude drugs accepted in one country are rejected in another. The methods of preparation and the tests for purity and quality are also far from identical. The weights and measures employed vary, as do also the thermometer and hydrometer scales. The languages, too, differ. The pharmacopœias of Austria, Prussia (V., VI. and VII. editions), Denmark (with a Danish supplement), Fennica (Finland?), Germany (1st ed.), Switzerland, Holland, Norway, and Sweden, are drawn up in Latin; the second edition of the German pharmacopœia is in Latin and German, the Latin being, as we are here informed, in part a mistranslation from the German; the Belgian is in Latin and French; the Greek is Latin and modern Greek with a Greek supplement; the Hungarian is written in Latin and Magyar; the British and the United States pharmacopœias are in English; that of France in French; and those of Roumania, Russia, and Spain in their own respective languages. Still, notwithstanding this diversity of tongues, we might expect the nomenclature both of plants and of chemical compounds to be approximately identical. Such, however, is far from being the case. The Spanish, and to some extent the French, pharmacopœia retain fragments of the terminology of the præ-scientific ages. The chemical nomenclature used by German pharmacists is very distinct from that employed in pure or in technical chemistry. Thus the reader would be apt to think that ferrum chloratum, bromatum, iodatum, &c., must mean iron chlorate, bromate, and iodate. But, on the contrary, these terms are applied unhappily, as it appears to us, to the chloride, bromide, and iodide. Further the term chloral is as well known in Germany as in England, but pharmaceutically speaking it receives the termination *um*, and figures as "chloralum."

This actually at one time was the cause of a misunderstanding and controversy. A company was at one time largely manufacturing and exporting aqueous aluminium chloride, under the name of "chloralum," for disinfecting purposes, and a German paper assumed that the agent used was a solution of chloral.

We find in this work no reference to an Italian or a Portuguese pharmacopœia.

Exercises on Mensuration for Junior Students. By T. W. K. START, Assistant-Master at the Manchester Grammar School. London: Sampson Low, Marston, and Co.

THIS pamphlet scarcely falls within the class of works of which we usually take cognisance. It is, however, undeniable that the ability to deal with such questions as are here given would be of great value to managers, foremen, &c., in chemical works.

CORRESPONDENCE.

ANALYSIS OF IRON.

To the Editor of the Chemical News.

SIR, — May I be permitted to say that I think Mr. Deane (CHEM. NEWS, vol. liv., p. 174) greatly underestimates the experience of the analysts engaged in our Iron and Steel Works. With regard to the separation of the silica from the solution of ore, pig, &c., in the gravimetric estimation of manganese, I have not heard of one analyst engaged in this class of work who would neglect such an obvious precaution. I know that I have not made such an estimation otherwise for ten years. And

not only this, but as a rule the Mn_2O_4 is carefully examined and any impurities found therein deducted. Volumetric methods, however, have, to a certain extent, done away with these tedious precautions, which are absolutely necessary for even a fairly accurate result.

In the estimation of phosphorus, where the precipitation by ammonium molybdate is made directly in the HCl solution of ore, metal, &c., it is my own practice, and that of most, if not all, analysts of my acquaintance, to have a measured excess of acid. To the HCl solution excess of NH_3 is added, then HNO_3 till the precipitate just dissolves, then a measured quantity of HNO_3 . The bulk of liquid, of course, is likewise measured.

The well-established efficiency of ammonium nitrate in hastening and completing the precipitation is evidently unknown to Mr. Deane.

I also notice that, although he gives the quantity of molybdate solution he uses, he omits to mention the strength of the solution, which is perhaps the most important point of all.—I am, &c.,

T. JOBSON, Jr., F.I.C.

Stocksbridge Works, Sheffield,
October 6, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 11, September 13, 1886.

Experiments on the Electro-Conductivity of Gases and Vapours.—Jean (probably Giovanni) Luvini.—The author's experiments lead to the conclusion that gases and vapours, under whatever pressure and at whatever temperature, are perfect insulators, and that they cannot be electrified by friction either among themselves or with solids or liquids. All theories relating to the electricity of machines, of the air, or of clouds, must be rejected as erroneous if it is admitted in them that moist air is a conductor, or that gases and vapours may become electrified by friction.

Determination of Dry Extract in Wines.—E. Bouillon.—Every augmentation of surface, e.g., by the addition of porous bodies, reduces the weight of the residue in notable proportions in consequence of the evaporation of a part of the glycerin. To obtain comparable results chemists ought to use a capsule with a flat bottom, of a standard diameter, placed quite level under the receiver of the air-pump, and containing always the same volume of wine.

No. 12, September 20, 1886.

Modern Kinetics and the Dynamism of the Future.—G. A. Hirn.—In a recent work bearing the above title the author presents in an accessible form all the arguments which render henceforth untenable the kinetic theory of gases, which refers the majority of the properties of these bodies to molecular movements. Among the arguments brought forward there are, says M. Hirn, at least three of such a kind that we shall one day be astonished how physicists have been, for a single instant, able to accept the kinetic theory of gases. The kinetics of gases might be correct without it following that light, radiant heat, electricity, magnetic attractions and repulsions, and gravitation are due to movements of ponderable matter, and still less that our thought is merely a molecular movement. But the converse is not true, and with the kinetic theory of gases fall the kinetic theories in general, which profess to explain all the possible phenomena of the universe by the invisible movements of matter. Two grand propositions confront each other in absolute antagonism.

According to one the movement of matter can arise only from another anterior movement and by immediate contact; according to the other motion never arises directly and by the immediate contact of matter and matter. The author contends that these two propositions, mutually exclusive, repose not upon metaphysical considerations, but upon the principles of applied and elementary mechanics; the demonstration of the one to the exclusion of the other is not to be banished to the land of dreams and chimeras, but is within the reach of all who occupy themselves with the reality of phenomena rather than with their *à priori* interpretation. The first proposition, and consequently all possible kinetic theories of which it is the starting point, fall with the kinetic theory of gases.

Biedermann's Central Blatt fur Agrikultur Chemie.
Vol. xv., Part 5.

Researches on the Proportion of Carbonic Acid in the Air.—W. Spring and L. Roland.—The air of Liege is exceptionally rich in carbonic acid, containing 0.05126 per cent by weight or 0.03353 by volume, as against 0.0483 and 0.03168 found in the air of Paris. The authors suggest that the cold weather of the earlier part of May may be due to a temporary decrease of atmospheric carbonic acid, occasioned by the demands of vegetation. In calm weather the air is, in the mean, poorer in carbonic acid than during strong winds.

Removal of Micro-organisms from Water.—P. Frankland.—From the *Proceedings of the Royal Society*.

Self-Purification of Foul Waters.—Prof. Alex. Müller.—The author observes that urine diluted with 100 parts of water is rapidly oxidised. Sugar, alcohol, and acetic acid check nitrification.

A Novel Theory of the Nutrition of Plants by Means of Fungi in the Soil.—Prof. Frank.—The author holds that the roots of most forest trees, oak, beech, birch, alder, and all the conifers have, in contradistinction to other trees, their roots clothed with a dense stratum of fungi, the capillary roots which, in other plants, effect the absorption of water and nutriment being entirely wanting. He considers that the fungus threads replace the capillary rootlets and mediate a direct assimilation of humus.

Hohenheim Manurial Experiments.—Prof. Strebel.—We find mention here of a "cock-chafer manure" prepared by Wolff and Sons, of Heilbronn. Its composition is not stated.

Use of Sugar in Feeding Fat Oxen and Young Cattle.—Prof. Holdefleiss.—One cwt. raw sugar seems to have been utilised to the value of 10s., which cannot be considered remunerative. Young cattle which received rations of sugar were injured in their health.

"Mal-Rouge" in Swine.—Schütz.—Swine can be protected against this disease by means of Pasteur's vaccine.

Determination of Metamorphic Products in Animal Dung.—Dr. Pfeiffer.—Not suitable for abstraction.

Formation and Migration of the Carbohydrates in the Leaves of Trees.—A. F. W. Schimper.—The mesophyll and the sheath cells exert an unequal attraction for dissolved carbohydrates.

Fluctuation of the Respiration of Plants.—G. Bonnier and L. Mangin.—From the *Comptes Rendus*.

Inequalities in the Composition of Gases in Leaves Exposed to Air.—S. Peyron.—From the *Comptes Rendus*.

Activity of Chlorophyll in Ultra-violet Darkness.—G. Bonnier and L. Mangin.—From the *Comptes Rendus*.

Quantities of Heat Liberated and Taken up by Plants.—G. Bonnier.—From the *Comptes Rendus*.

Composition of Potatoes when not Fully Ripe.—F. Hungerbuehler.—As ripeness progresses the propor-

tions of starch and of non-albumenoid nitrogen increase, whilst that of albumenoid nitrogen decreases.

Application of a Mixture of Quicklime and Blue Vitriol against Mildew in Vines.—E. Prillieux.—The results were generally found satisfactory. The proportions used were 25 kilos. copper sulphate in 225 litres water and 25 kilos. quicklime.

Copper contained in Vines treated with the Mixture of Lime and Copper.—A. Millardot and U. Gayon.—The wines contained traces of copper doubtful or too small to be determined. The maximum was 0.1 gm. in 100 litres.

Action of Pasteurising upon Milk.—Dr. J. Van Geuns.—This process consists in heating the milk for a short time to 62°. By this means the lactic fermentation is retarded for some days. By far the greater number of the microbia are killed.

Classification of Wines.—A. W. von Babo.—The author divides wines into six classes:—(1) "Ausbruch" wines (a kind for which there is no English name); they are so concentrated that a complete decomposition of the sugar into alcohol and carbonic acid cannot take place, much of it remaining in the wine unchanged. Such wines contain little acid, a high proportion of extract, and not more than 14 to 15 per cent of alcohol. (2) Liqueur wines are those where the complete decomposition of the sugar is prevented by the direct addition of alcohol. They contain 18 to 24 per cent of alcohol and a less proportion of extractive matter than do the Ausbruchs. (3) Bouquet wines are of an acidulous flavour, and in them a normal decomposition of the sugar has taken place. Their value depends on ethereal compounds. The celebrated products of the Rhine district belong to this group. (4) Heavy table wines have a full flavour without sweetness. They have little acidity. The Austrian and (ordinary) Hungarian wines belong here. (5) Light dinner wines. They contain little acidity and are not strongly alcoholic. They are of great importance in commerce, but rarely receive prizes at exhibitions. (6) Labourers' wines with little alcohol and extractive, but much acid. Petiotised wines fall in this section.

New Experiments on the Fermentation of Urine.—Prof. A. Müller. The author ascertains the action of a number of substances in promoting or retarding the fermentation of urine. It appears that potassium permanganate promotes fermentation, whilst potassium chlorate delays it.

Preservation and Disinfection of Blood.—Prof. A. Müller.—The author recommends peat-mull and lime for working up blood into manure. Manganese chloride and hydrochloric acid are less efficacious in preventing nuisance than free sulphurous acid. Sulphites are less efficient.

MISCELLANEOUS.

Science Works.—We have received from Mr. W. F. Clay, of Edinburgh, two catalogues of standard scientific books which appear to be offered at very cheap prices, and we should advise those of our readers who want an opportunity of stocking their libraries to send for these catalogues. More than ordinary interest will be attached to many of these works from the fact that they formed a portion of the library of the late Dr. Henry Watts, F.R.S.

Prize to Chemists.—The money prize open for competition three months ago, by the Canadian Meat Company, of Liverpool, London, Montreal, Chicago, Boston, and New York, has been awarded to Dr. A. B. Griffiths, F.R.S. (Ed.), F.C.S. (Lond. and Paris), Head Master and Lecturer on Chemistry, School of Science, Lincoln, and to Baron Romburg,—for their essays on the scientific and medical value of the Company's "Extract of Beef."

TO CORRESPONDENTS.

Ignoramus.—Certain experiments have been lately made under the direction of Prof. Holdefleiss (*Organ des Central Vereins für Rüben Industrie der Oester. Ungar. Monarchie*, vol. xxxiii., p. 779). A number of bullocks were fed with a diet of beets, clover and lucerne, hay, rye and barley-straw, rape-cake and bran. Two of them received in addition 0·75 to 1 kilo. sugar daily. The average increase of weight in those receiving the sugar was 137·5 kilos in 114 days, whilst those without sugar increased on the average only 102 kilos. in the same time.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1404.

ON THE MAGNETIC ROTATION OF MIXTURES OF WATER WITH SOME OF THE ACIDS OF THE FATTY SERIES, WITH ALCOHOL, AND WITH SULPHURIC ACID, AND OBSERVATIONS ON WATER OF CRYSTALLISATION.*

By W. H. PERKIN, Ph.D., F.R.S.

FROM the author's previous work on the magnetic rotation of compounds it was found that the molecular magnetic rotation of water, which is taken as unity, is not the same as the sum of the values of oxygen and two of hydrogen, as deduced from the molecular magnetic rotation of other bodies. Thus hydrogen is found to be 0.254, whilst hydrogen in hydroxyl varies from 0.194 in ordinary alcohol to 0.137 in monobasic acids, and is 0.261 in carbonyl, so that taking the lowest number it gives $H_2 + O = 0.645$, and taking the highest it is 0.769.

From these facts it appeared that the determination of the magnetic relation of hydrated bodies might give numbers which would show whether they contained water, or whether the substances with which it was mixed had combined so as to form new compounds. If the former were the case the molecular rotation should represent that of the compound + that of water; if the latter, it should be lower than this: for example, if formic acid were mixed with water, molecular proportions being used, either $H.COOH + H_2O$ or $H.C(HO_3)$ might be produced. In the first case the rotation should be—

Formic acid	1.671
Water	1.000
	2.671

In the second, taking the highest value of $H_2 + O$, it would be—

Formic acid	1.671
Water	0.769
	2.340

which is considerably lower.

As some of the fatty acids have been believed to unite with water, to form trihydric alcohols, they were selected for examination, and at the same time hydrated alcohol was also examined, because it could not form a compound with water, and would therefore act as a check upon the results.

The results of the examination show that formic, acetic, and propionic acids, when mixed with water, do not form new compounds, but that the products simply consist of these bodies and water.

Sulphuric acid in the pure and its hydrated conditions was next examined, viz., H_2SO_4 , $H_2SO_4 + H_2O$, $H_2SO_4 + 2H_2O$, and $H_2SO_4 + 3H_2O$. The numbers obtained in this case show that combination takes place chiefly when one molecule of water has been added only to a small extent in the case of the second addition, and scarcely any when the third is added; and the author gives reasons for considering that sulphuric acid combines with one molecule of water only, forming the compound $(HO)_4SO$.

Whilst studying the nature of the hydrated products, the author's attention was drawn to the subject of water

of crystallisation, and from the inconsistency as to the presence or absence of water of crystallisation in compounds of the same class,—as, for example, in those of silver, potassium, and sodium, and also methyl bromide as compared with analogous compounds,—he considers it impossible to believe that water of crystallisation has any relationship to chemical combination; that of course refers to water when it exists as such, and not to hydrogen and oxygen present in the proportions found in water but otherwise combined. If this be so, it is thought that its association with chemical compounds is most likely connected with the building up of the crystalline form, it being difficult to see what other part it can play; and the reason why some compounds crystallise without and some with water of crystallisation is probably determined by the tendency to produce that form which can be the most readily built up; if that can result from the anhydrous salt, anhydrous crystals are formed; if with the salt and water, then it will contain water of crystallisation; and it is well known how change of conditions will cause variation in the proportions of water of crystallisation, and also form of crystal.

These observations would also apply to compounds crystallising with alcohol, acetic acid, benzene, &c., and to some double salts where one or more of the constituents would act like water of crystallisation. Attention is drawn to the fact that if the above view of water of crystallisation be correct, it is evident that a salt containing water of crystallisation will be resolved into water and the salt on breaking up of the crystalline form by solution, which is believed to be the case by many who have studied the subject of solution.

ON THE NATURE OF LIQUIDS.

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

WE read a short paper with the above title to the Chemical Society last June, embodying certain results which we had obtained during the past few years; and as our conclusions have, since the presentation of that paper, received striking confirmation by the Natansons, during a research on the vapour-densities of nitrogen peroxide, it appears to us advisable to bring these results before the Association as a contribution to the discussion on "Solution;" for it is evident that no theory of solution can be more than tentative which is not based on some definite conceptions of the actual nature of the menstrea in which solution takes place.

There will shortly appear, in the *Philosophical Transactions of the Royal Society*, a memoir on the behaviour of alcohol when heated. In this memoir we give data which we have deduced:—the expansion of liquid alcohol, between the temperatures of 13° and its critical point 243.1° ; the compressibility of the liquid at various temperatures; the density of the unsaturated and saturated vapour; the vapour-pressures, from which have been calculated the values of increase of pressure for unit rise of temperature at certain definite intervals of temperature; and from these data the heats of vaporisation of the alcohol have been calculated. Last May a paper embodying similar results was read before the Royal Society, on ethyl ether; and a paper has recently been published in the *Transactions of the Chemical Society* on acetic acid. We have since finished a similar research on methyl alcohol, and we propose to extend this inquiry to the homologous alcohols.

The chief point which we have to deal with here is the densities of the saturated vapours of these bodies, at definite intervals of temperature, for from these data our deduction as to the nature of liquids is drawn.

* Discussion on the "Nature of Solution," British Association, Birmingham Meeting, Section B.

* Discussion on the "Nature of Solution," British Association, Birmingham Meeting, Section B.

Now we find that the density of the saturated vapour of ethyl alcohol, of methyl alcohol, and of ethyl ether, under a pressure of 760 m.m., is somewhat greater than that deducible from their molecular formulæ. This is no new discovery; it has been long known that the density of a vapour near its condensing-point was somewhat abnormal. It has been investigated for water by Fairbairn and Tate, and for some other liquids by Schoop. But it has, we think, not been previously noticed that with such liquids, the chemical nature of which would not lead us to conjecture the union of their simple gaseous molecules to form a complex molecule, the density of the saturated vapour decreases with fall of temperature, and corresponding fall of pressure; and indeed becomes normal, and calculable from the respective molecular formulæ, at a pressure of about 200 m.m. Again, with rise of temperature, and corresponding rise of pressure, the density of the saturated vapour of such bodies rises, and, increasing with regularity, becomes at the respective critical points equal to that of the liquid, which has been enormously expanded by rise of temperature. If density be mapped on curve-paper as ordinates, and pressure as abscissæ, the relation of the saturated densities of such liquids is represented by a regular curve, the region where double flexure occurs being at a pressure of about 1000 to 5000 m.m., the temperature depending naturally on the nature of the liquid.

As we have remarked, we have also investigated within wide limits the changes produced by heat on acetic acid. The critical temperature of acetic acid lies too high for accurate measurement with the means at our disposal. But we have traced the relation of pressure to density so far as to show that with rise of pressure, and corresponding rise of temperature, the density of the saturated vapour is increasing rapidly. The limit of temperature employed by us was 280°. The isothermal representing densities of the unsaturated vapour at that temperature shows a little increase of density from a little above the normal density (30, where $H=1$) at pressures below one atmosphere to 25,000 m.m., when the pressure is equal to that of the vapour in contact with liquid. It cannot be doubted that had we had the means of employing still higher temperatures, we should have found the density of the saturated vapour increase until the critical point was reached. With fall of pressure the density of the saturated vapour decreases, until at 140° the vapour is about fifty times as heavy as hydrogen under the same conditions of temperature and pressure. Little change takes place during a considerable fall of pressure, but at a certain pressure—corresponding to a temperature of about 120° to 130°—the vapour-density begins evidently again to rise, and continues to increase with fall of temperature and pressure, until at 50°—the lowest temperature and pressure at which we were successful in measuring this quantity—it had risen to 57 to 58.

Here we have a striking difference between ethyl alcohol, ether, and methyl alcohol, on the one hand, and acetic acid on the other.

These results have been confirmed by work which has lately been published by the Natansons. By a very ingenious method they have investigated the density of the unsaturated vapour of nitric peroxide. As these results have not been published in English, it may be advisable here to give some of the figures which they quote, transferring, however, their numbers, which refer to air as unity, to the basis of hydrogen. They give an isolated observation at -12.6°, and seven isothermals at 0°, 21.0°, 49.7°, 73.7°, 99.8°, 129.9°, and 151.4°. This limit of pressure was 800 m.m. Now the boiling-point of nitric peroxide at 760 m.m. is from our measurements (*Phil. Trans. Royal Society*, in course of publication) 21.8°, and the densities of the saturated vapour are deducible only from the first three of his isothermals. We have plotted their results on curve-paper: this has shown the great regularity and trustworthiness of their observations; and by continuing the curves in the direction in which they run, until they intersect the straight

lines denoting vapour-pressures at the temperatures at which their measurements were made (using for this purpose the vapour-pressures determined by us), the density of the saturated vapour is determined with but small error.

The Natansons' numbers are as follows:—

Temp.	Press.	Density.	Temp.	Press.	Density
-12.6°	115.4	52.54	21°	491.6	38.74
0.0	37.96	35.84		516.96	39.01
	86.57	38.59		553.50	39.15
	172.48	40.71		639.17	39.64
	250.66	41.90			

At -12.6° the vapour-pressure of nitric peroxide is 125 m.m.; it must therefore nearly represent the density of the saturated vapour. At 0° the vapour-pressure is 255 m.m.; again the density found by Natanson must be nearly that of saturation. At 21° the vapour-pressure is about 700 m.m., and a prolongation of the curve constructed from the above numbers would cut the horizontal line representing the large alteration of volume with no rise of vapour-pressure, at a vapour density of about 40. It is evident therefore that with nitric peroxide, as with acetic acid, the density of the saturated vapour increases with fall of pressure and temperature. Now it is known that nitric peroxide dissociates, for the physical properties (colour, &c.) change, on change of N_2O_4 into $2NO_2$, and the similarity of behaviour between nitric peroxide and acetic acid renders the dissociation of acetic acid from $(C_2H_4O_2)_n$ into $nC_2H_4O_2$ no longer conjectural.

We have, then, to consider what reason can be ascribed to account for this behaviour. All liquids, dissociable or stable, show an increase in the density of their saturated vapours above a certain pressure and temperature, differing, of course, for each liquid. Some liquids, known to be dissociable into simpler molecules, show an increase, both on rise and on fall of temperature and pressure, above and below a certain temperature and pressure peculiar to the liquid. Now it is known that a high temperature favours dissociation. Hence it may be expected that the increase of the density of the saturated vapour universally observed at high temperatures should be explicable not on the hypothesis that such high pressures promote combination, because the corresponding high temperature would be extremely unfavourable to combination, but on the theory that, in spite of the tendency of the high temperature to separate the molecules from each other, they are nevertheless forced into close proximity by the corresponding high pressure. On the other hand, a low temperature is known to favour stability. Hence bodies consisting of molecules capable of chemical combination with each other, such as nitrogen peroxide and acetic acid, might be expected to give, as they do, evidence of such combination at low temperatures, in spite of the corresponding low pressure. It is impossible to conclude that the same effect should be produced, as it were, at each end of the scale of temperature, under such totally opposite conditions, by the same cause; and, inasmuch as bodies—such as ethyl and methyl alcohol and ether—exhibit no trace of such increase of the density of the saturated vapours with fall of temperature and pressure, it must, in our opinion, be concluded that the difference between gases and liquids lies merely in the relative lengths of the free paths of the molecules in the two states, and that, provided temperature and pressure are both sufficiently low, the body assumes the liquid form, and exhibits surface tension and cohesion, owing to the attraction of any one molecule for every other molecule,—not of any definite set of molecules for each other, which would result in the formation of a complex molecule. In short, the molecules of stable liquids exhibit physical attraction and not chemical attraction; the molecules of dissociable liquids exhibit *qua* liquids physical attraction, but they also exhibit chemical attraction, inasmuch as they tend to unite in pairs, or perhaps in simple groups.

We have another argument which goes far to prove this theory. If, at any given temperature, the relations between pressure and density of the unsaturated and saturated vapour of a stable substance be followed out, it has been found by us that the moment liquid is visible, at that moment the pressure is the vapour-pressure corresponding to the temperature; but on the contrary, with acetic acid, liquid may be present in a condensed form in small amount, and yet the pressure continues to rise with decrease of volume and corresponding condensation of more liquid. This can easily be explained on the supposition that the body under experiment is not homogeneous. With a little condensed liquid present the molecules of higher molecular weight are partially condensed out, and the vapour remaining retains proportionally more of the body with lower molecular weight, which may well be supposed to possess a lower boiling-point, or, in other words, to exert a higher pressure at any given temperature. Condensation proceeds, the condensed body consisting largely of the more complex molecules, and hence pressure rises correspondingly. The case is somewhat analogous to the compression of a mixture of the vapour of a stable substance with such a gas as hydrogen; but of course this instance exhibits this behaviour on an exaggerated scale. The data given in our paper will prove satisfactorily the complete absence of air and impurity, which, of course, would produce a similar result. It may be therefore concluded that, as stable liquids show no sign of this behaviour, their molecules show no tendency to combine so as to form complex molecular groups.

It is of course still open for any one to state that when the vapours of stable liquids condense, combination to form complex molecular groups, or chemical combination, occurs *precisely at the moment of condensation*. This we have not absolutely disproved; but we think that the foregoing experiments render such a hypothesis, to say the least, improbable, and the onus of proving it must be borne by those who would make the assertion.

Last year we made some experiments with the view of testing solubility in a fluid above its critical point. It will be remembered that some years ago Mr. J. B. Hannay worked at this subject, and stated that the fluid retained the power of dissolving solids; that on compression the solvent power increased; and that on warming evenly, so as to rarify the fluid, the solid was deposited. In our experiments the solid employed was eosine, and the liquid was alcohol. It is well known that a solution of eosine has a given fluorescence, whereas the solid is a dark red substance. It was supposed that the state of solution could be tested by the permanence of the fluorescence. We noticed that the fluorescence notably decreases at temperatures approaching the critical point; but that it is still permanent, at least for a short time, at temperatures a little above the critical point, and at volumes smaller than the critical volume. The difficulty of observation is, however, so great that we cannot positively state whether the solid is permanently retained by the fluid above the critical point; our impression is that after some time it is wholly deposited as a solid on the walls of the tube. It is extremely difficult to detect fluorescence in a tube the sides of which are coated with a translucent red deposit. From our view of the nature of liquids it is to be expected that solution should continue above the critical point, provided the volume is sufficiently small.

The Butylic Ethers of the Mono- and Dichloroacetic Acids.—G. Gehring.—Butyl monochloracetate is a colourless, very mobile liquid, of a pleasant fruity odour and a burning taste. It dissolves in alcohol in all proportions and is sparingly soluble in water. Its sp. gr. at 0° is 1.103, and at 15° 1.081. The dichloroacetate is colourless and very mobile; its odour is less pleasant than that of the corresponding mono-compound, and its taste is scarcely burning. It boils at 184°, and its sp. gr. at 0° is 1.182 and at 15° 1.169.—*Bull. de la Soc. Chim. de Paris*.

ON THE
ACTION OF HYPOCHLOROUS ANHYDRIDE
ON IODINE TRICHLORIDE.

By H. BASSETT and E. FIELDING.

THE following experiments were undertaken for the purpose of testing the possibility of a direct combination of the two reagents, which might have led to the formation of an oxychloride of iodine corresponding to pentabasic periodic acid.

The reaction taking place, however, is totally different, but we considered the results obtained of sufficient interest to be recorded.

The first experiments were made as follows:—

Two grms. iodine dissolved in 10 c.c. tetrachloride of carbon, and dry chlorine passed into it till saturated, when ICl_3 was deposited as an orange-coloured powder. In another bottle was placed 4 grms. dry precipitated mercuric oxide, covered with 30 c.c. CCl_4 , which was then also saturated with dry chlorine, with frequent agitation. After standing a short time to settle, the clear liquid was poured into the solution of ICl_3 , when an abundant flocculent precipitate was produced, of a light buff-colour, and the ICl_3 gradually disappeared on agitation. After a time the precipitate collected at the bottom, leaving the solution only slightly coloured. Similar results were obtained when the experiment was made in a different way, *i. e.*, by passing a slow current of Cl_2O through the solution of ICl_3 .

A stream of dry air was then passed through the bottle, at first cold, till the excess of Cl_2O was expelled, and then heated to 100°, or rather more, when the CCl_4 slowly distilled off, together with orange-coloured vapours of chloride of iodine, at last leaving a buff-coloured, solid, powdery residue. Heated strongly in a tube this substance gave off at first a small quantity of reddish vapour, and at a still higher temperature a large quantity of iodine sublimed, and the tube was found to be full of oxygen.

Several analyses of the substance prepared in this way gave results indicating that the main product of the reaction is iodic anhydride, retaining, however, varying quantities of ICl_3 .

We may here suggest that the above-mentioned solution of Cl_2O in CCl_4 may perhaps find applications in other cases.

We then tried the action of gaseous Cl_2O on the solid ICl_3 , in the following way:—Chlorine, dried by H_2SO_4 and CaCl_2 , was passed through a number of tubes drawn out at both ends, and containing a few grammes of dry iodine till completely saturated, and the tubes then sealed up till required.

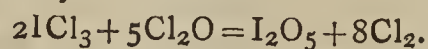
A very slow current of Cl_2O (prepared by passing dry chlorine over mercuric oxide previously heated for an hour or more to 250°, in a tube rather more than a foot long, kept cool by water) was then passed through two or three of these tubes connected end to end; from the last tube the excess of gas was conducted into a cylinder containing hydrate of lime.

After a time the ICl_3 became gradually paler in colour, in some places nearly white; but the action is very slow, and even after many hours is only partial, the inner portion escaping the action of the gas.

The excess of ICl_3 was then expelled by placing the tubes in a trough of boiling water and sending a current of dry air through them. Large quantities of vapour of chlorides of iodine then came off, and after a considerable time the contents of the tubes were reduced to a comparatively small quantity of a nearly white, hard, amorphous residue. The last traces of ICl_3 were only got rid of with difficulty.

The residue thus obtained dissolves in water, forming a colourless solution of iodic acid quite free from chlorine if the heating, &c., has been of sufficient duration.

The reaction may be written—



We satisfied ourselves by experiment that a considerable evolution of chlorine actually takes place, by passing the gas issuing from the reaction tube through a solution of the brown monochloride of iodine in CCl_4 . In a short time a deposit of the orange-coloured ICl_3 was formed, while the Cl_2O before traversing the reaction tube was found to produce no apparent change,—in itself an interesting and rather unexpected fact.

The substance thus obtained was analysed by dissolving a weighed quantity in excess of carbonate of soda, acidifying with nitric acid, and precipitation with nitrate of silver, and weighing the total iodate of silver with the filter dried at 100° . The bulk of it was then detached from the filter and weighed in a bulb tube with a long neck, then heated in an air-bath to 180° or so, when a further slight loss of water takes place. Then, after weighing again, heated carefully over a lamp till the evolution of oxygen completely ceased, leaving a residue of fused iodide of silver, and finally weighed. From the loss of oxygen the percentage of I_2O_5 was then calculated.

Two different preparations gave in this way 97.6 and 97.1 per cent I_2O_5 , numbers which may be taken as sufficient to establish the nature of the reaction, considering the difficulty of drying the very large volumes of gas and air passed over the product.

Our best thanks are due to Mr. F. A. Manning for the use of his Laboratory.

THE LAW OF VOLUMES IN CHEMISTRY.

By T. STERRY HUNT.

THE questions regarding the so-called molecular weights and volumes of liquids and solids, which are now attracting the attention of chemists, can, I think, be better understood if we keep in mind the principles enunciated by the writer in 1853, that "the doctrine of chemical equivalents is that of the equivalency of volumes," and that "the simple relations of volumes which Gay-Lussac pointed out in the chemical changes of gases apply to all liquid and solid species;" so that "the application of the atomic hypothesis to explain the law of definite proportions becomes wholly unnecessary." In further illustration of this view, it was said in 1867 that "the gas or vapour of a volatile body constitutes a species distinct from the same body in a liquid or solid state; and the liquid and solid species themselves often [probably always] constitute two distinct species of different equivalent weights." From this it follows that freezing, melting, and vaporisation are chemical changes. The union of many volumes of a vapour or gas in a single volume of a liquid or a solid is a process of chemical combination, while vaporisation is chemical decomposition. Such decomposition is either with or without specific difference, and examples of these two modes are seen respectively in heterogeneous dissociation and in integral volatilisation, which latter is the breaking-up or dissociation of a polymeric species into simpler forms having the same centesimal composition. Both of these processes are subordinated to the same laws of pressure and temperature, and involve similar thermic changes in the relations of the bodies concerned. In this enlarged conception of the chemical process we find a solution of the problems above named, and an explanation of the distinction which has been made between "the chemical molecule" and "the molecule of the physicist." That the latter has a much less simpler constitution than the former, as calculated from the results of chemical analysis and from vapour density, has been long maintained alike on dynamical and chemical grounds. It is discussed by the

writer in 1853 in the Essay already quoted, entitled "The Theory of Chemical Changes and Equivalent Volumes,"* and again in the late paper of Spencer Pickering in the CHEMICAL NEWS, November, 1885.

If, then, as maintained by the writer, the law of volumes is universal, and if the production of liquids and solids by the condensation of vapours is a process of chemical union giving rise to polymers, the equivalent weights of which are as much more elevated as their densities are greater than those of the vapours which combine to form them, the hypothesis of atoms and molecules, as applied to explain the law of definite proportions and the chemical process, is not only unnecessary, but misleading. According to this hypothesis, which supposes molecules to be built up of atoms, and masses of molecules, the different ratios in unlike species between the combining weight of the chemical unit or molecule (as deduced from analysis and from vapour density; $H=1.0$) and the specific gravity of the mass are supposed to represent the relative dimensions of the molecule. Hence the values got by dividing these combining weights by the specific gravity have been called "molecular volumes." The number of such molecules required to build up a physical molecule of constant volume would, according to this hypothesis, be inversely as their size. If, however, as all the phenomena of chemistry show, the formation of higher and more complex species is by condensation, or, in other words, by identification of volume, and not by juxtaposition, it follows that the so-called molecular volumes are really the numbers representing the relative amount of contraction of the respective substances in passing from the gaseous to the liquid or solid state, and are the reciprocals of the coefficient of condensation of the assumed chemical units. If steam at 100°C . and 760 m.m. pressure, with a formula, as deduced from its density, of H_2O , and a combining weight of 18, is converted into water at the same temperature, 1628 volumes of it are condensed into a single volume, having a specific gravity of 0.9588, which at 4°C . becomes 1.0000. Water is thus $1628(\text{H}_2\text{O})$; and the weight of its volume at the temperature of formation, as compared with an equal volume of hydrogen gas or of steam,—in other words, its equivalent weight,—is $1628 \times 18 = 29,304$, which thus corresponds to a specific gravity of 1.0000; ice, at its temperature of formation, with a specific gravity of 0.9167, being $1487(\text{H}_2\text{O})$, with an equivalent weight of 26,766. The hydrocarbon, $\text{C}_4\text{H}_{10}=58$, condenses to a liquid having—according to Pelouze and Cahours—a specific gravity of 0.600, which corresponds to an equivalent weight, as compared with that of water, of 17,582, or approximately $303(\text{C}_4\text{H}_{10})$, with a calculated specific gravity of 0.5997. The reciprocal of the coefficient of condensation (or so-called molecular volume) of steam is 18, while that of the gaseous hydrocarbon is—

$$600 : 1000 :: 58 : x = 96.66.$$

The chemical unit for bodies which, like these, volatilise integrally, is fixed by the density of their vapours; while for fixed species, like anhydrous oxides and silicates, or for those which by heat undergo heterogeneous dissociation, as, for example, calcite and hydrous silicates, the unit may be the simplest formula deduced from analysis, or, for greater convenience in calculation in the case of oxides and silicates, may have a value corresponding to $H=1$, or $O=8$. The unit for silica thus becomes $\text{SiO}_2 \div 4 = 15$; that for alumina, $\text{Al}_2\text{O}_3 \div 6 = 17$; and that for the magnesian silicate, $\text{SiMg}_2\text{O}_4 \div 8 = 17.5$. Such unit-weights as these have been employed by the writer in his late Essay on "A Natural System in Mineralogy," in the tables of which they are represented by P; while the values got by dividing these numbers by the specific gravity of the species have been designated "unit volumes," and represented by V. The writer of that Essay, in de-

* See the author's "Chemical and Geological Essays," pp. 426 to 437, and further, *ibid.*, pp. 453 to 458.

ference to the general usage of chemists, therein adopted the received terminology of "molecular weights" and "molecular volumes," and, failing at the time to grasp the full significance of his own earlier teachings as to the universality of the law of volumes, spoke of the so-called molecular weight as an unknown quantity, although in accordance with that principle this molecular weight, or, properly speaking, this equivalent weight, is simply deduced for any body the specific gravity of which is known.

Centre Harbour, N.H., Sept. 3, 1880.

COUNTER-EXPLANATION AND COMMUNICATION OF FURTHER EXPERIMENTS ON THE CERIFEROUS HAINSTADT CLAYS.*

By Dr. JONAS RUDOLPH STROHECKER.

SINCE criticism has taken the author's analytical results as its object, and as the continuation of his investigation of the precious Hainstadt material has led to important and novel results, he ventures upon a criticism of the present point of view in the chemistry of the rare earths. The criticism of other chemists on his analyses and his own observations on the Hainstadt cerium in its various stages of oxidation (CeO , Ce_3O_4 , and Ce_2O_3 , the atomic weight being taken as 92.1) come here into consideration; the remaining rare earths, on account of their unequivocal behaviour, require no reformatory communication.

A. Schertel, of Berlin, and Prof. Blomstrand, of Lund, have come forward to criticise the author's analyses. The former judges without practical experience, and admits on p. 1368 of the *Berichte* (1886) that he has not found the rare earths. The Hainstadt clays are very numerous, and Herr Schertel may have obtained specimens free from cerium. Prof. Blomstrand, the most experienced of the Scandinavian mineral chemists, seems to have been in the same case. The critics, however, have come too late, for before their papers could be read considerable quantities of chemical preparations from the Hainstadt cerium clays have been sent into the wide world for experimental purposes, especially lanthanum and yttrium salts. No practical use has hitherto been made of the didymium which occurs only sporadically in the clay bed II. Cerium preparations from cerite have hitherto been preferred to those from the Hainstadt clays, since in the latter cerium occurs in the state of $\text{Ce}_2(\text{OH})_6$, which is less readily separated from iron, whilst in cerite it occurs as CeO , which is very easily freed from this impurity. This hindrance is now removed.

Cerium is contained in the clay beds I. and II. as hydroxide, as appears from the following facts:—The non-bituminous flesh-coloured clay No. I. yields at a red-heat bricks coloured orange-red by anhydrous Ce_2O_3 very distinct in their colour from bricks coloured by ferric oxide, and it is thus well-characterised by its own colouration. In its hydrochloric extract, as in that of the unignited black clay II. *a* ammonia yields a reddish brown precipitate which at first sight may be mistaken for ferric hydroxide. But if the clay II. *a* is ignited so that its carbon reduces Ce_2O_3 to Ce_3O_4 , the ammoniacal precipitate is of a lemon-yellow ceroso-ceric hydroxide, a fact which has escaped the critics. In the exsiccator the water of hydration remains in both the cerite clays but escapes on heating, leaving orange-red Ce_2O_3 , which, in the clay II. *a*, is reduced to the light yellow Ce_3O_4 , which becomes brilliantly incandescent, another fact overlooked by the critics.

The solubility of the Hainstadt cerium hydroxide in caustic alkalies is easily demonstrated if the non-

bituminous clay No. I. is added in fine powder to a saturated boiling potash or soda-lye and strongly boiled for two days in a covered iron pot, or by putting Ce_2Cl_6 in a strong boiling lye, or by decomposing cerium-alum by a colourless caustic lye in the cold. In all three cases the reaction of Ce_2O_3 is to be recognised in the liquid. We come now to the question of the great similarity of the ammonia precipitate from the hydrochloric extract of both the ceriferous clays and from ferric salts. This is due to the circumstance, already put on record in the literature of cerium, that its oxides change their colours strikingly in presence of small quantities of impurities. As the red-brown colour of dry ferric hydroxide may also be called flesh-colour, and actually is (1), it is intelligible how traces of ferric oxide, mixed with $\text{Ce}_2(\text{OH})_6$, may give the latter the dark colour of an ordinary ferric precipitate. The iron in a cerium solution completely masks its ferro-cyanogen reaction, and in heat the pale yellow ferrocyanic precipitate of C_2O_3 becomes blue on regular acidulation.

To separate perfectly Ce_2O_3 from Fe_2O_3 is practicable only by converting the former into cerium sal-ammoniac, which leaves behind all the iron. It can be readily separated as sulphate, but retains iron, which is simultaneously carried down. The same result occurs in attempts at separation with potassium sulphate, and with oxalic acid it is not precipitated at all.

If it is desired to separate cerium from iron by means of oxalic acid it must be present as CeO or Ce_3O_4 , or be reduced to these states. Carbon and caustic potash must be used. The addition of carbon is not necessary in the clay II. *a*. If $\text{Ce}_2(\text{OH})_6$ from either clay, still retaining its iron, is fused with caustic potash, it is converted with escape of oxygen into yellow $\text{Ce}_3(\text{OH})_8$, which, if heated in contact with the air while still moist, is instantly turned to a leather-brown colour. In this state the oxide evolves chlorine with hydrochloric acid, in proof that Ce_3O_4 is still present along with Ce_2O_3 . As ferri-ferrous $\text{Ce}_2(\text{OH})_6$ is also reduced by heating with soda, this process may be used to separate it from iron. The mass, when cold, is dissolved in hydrochloric acid, and the filtrate, while still hot, is precipitated with potassium oxalate. The cerous oxalate thus obtained passes, by gentle ignition, into lemon-yellow anhydrous Ce_3O_4 , and this again, on further heating, into the orange-red anhydrous Ce_2O_3 , the cheap preparation of which, as a painters' colour, is now in prospect. At a white heat the colour changes to a leather-brown. The cause of this colour appearing in bricks is not so much the presence of iron as that of an unreduced portion of Ce_2O_3 . It cannot be assumed that the presence of lanthanum has an effect on the colour of the bricks.

A further point is the blue melt which caustic potash produces with the clay I., and with the ferri-ferrous $\text{Ce}_2(\text{OH})_6$, obtained from both clays. According to previous traditions it must have been regarded as a solution of CeO in potash, since CeO is the only blue stage of oxidation. But this view could not be verified. As manganese occurs only here and there in very slight traces in the Hainstadt clays, and as the colour of the melt is different from that of this metal, it may remind us of CeO_3 , ceric acid. But there was a difficulty in admitting a ceric acid; on attempting to obtain pure $\text{Ce}_2(\text{OH})_6$ from the ferri-ferrous product by extraction with hot ammonium carbonate there was obtained the above-mentioned flesh-coloured preparation. But this, if fused with alkali, gave not a blue but a light flesh-coloured melt, so that the element which is the basis of the blue compound cannot be the cerium extract.

What element is here present is not known to the author. The like must be said of the sky-blue matter separated on adding potassium hydroxide to the solution of a cerium salt, as well as of the steel-blue colour of the ignited mass. As the unknown element was contained in the cerite oxides as precipitated by potassium sulphate we have here a *proserpinium* if the metal approximates to

* Reprint from *Technische Mittheilungen für Malerei*, courteously forwarded by the Author.

cerium, or a *quirinium* if the metal found in the Hainstadt clays approaches iron. It is also possible that cerium, like didymium, may be resolved into two metals. A further observation refers both to cerium and iron. In preparing the flesh-coloured compound, $\text{Ce}_2(\text{OH})_6$, by means of ammonium carbonate it appears that the reddish brown liquid floating above the precipitate, and containing cerium and iron in molecular distribution, reddens blue litmus, thus rendering intelligible the solubility of the Hainstadt $\text{Ce}_2(\text{OH})_6$ in caustic alkali.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from p. 197.)

In the study of the nature of minerals, according to optical methods, we can make use of prepared specimens as soon as they have had any adhering Canada balsam cleaned off, and these specimens can be preserved for an indefinite time. All modifications in the methods of examination naturally arise from changes effected in the apparatus employed; if we assume that this fulfils certain necessary conditions the specimen has to undergo no other manipulation beyond being removed from the object stage of the microscope. Further, if we consider that microscopic examination, as it has been developed by the work of Sorby, Zirkel, and Vogelsang, enables us to arrive, in the space of a few minutes, at a definite solution of several questions which could not be answered by a mere inspection of the sample, and that microscopic specimens of rocks prepared in thin plates are equally as good as animal or vegetable specimens both in sharpness of detail and beauty of colouring, we can easily understand why naturalists have a leaning towards optical methods of examination. The study of minerals by these means is a most convenient one, when carried out by the aid of excellent apparatus, and it enables us to submit the matter in question to most searching enquiry, and to determine its nature without injuring the specimen, and, in addition, this method takes but little time and is easy to carry out.

The determination of minerals according to their form and their physical properties, brought to perfection by the work of Werner and Mohs, even to forming a complete system, was obliged to give way to a method of research based on the application of chemical reactions. However, in modern micro-mineralogy, these older methods have again acquired a preponderating value, having some particular properties which result from the conditions under which thin plates of minerals, cut in any direction, may be studied.

Among the minerals which may be sliced in this manner is very rare that substances entirely opaque are found; but among those which are, magnetic iron ore, titaniferous iron, and pyrites may be mentioned.

The influence of the inequality of planes and the opacity of matter, which so often interfere with the use of the zoniometer, and of M. Kobell's stauroscope, is diminished or entirely removed by the use of extremely thin plates, and as to the direction of cleavage, which is generally found by using a hammer and chisel, it is nearly always indicated by parallel cracks.

Interposed matter has only attracted the attention of mineralogists after the use of the microscope became general. These allied matters are so characteristic of some minerals that their presence helps the recognition of certain species, such as haüynite, nosite, leucite, quartz, garnet, &c.

In cases where optical means cannot be employed the microscopist is at a disadvantage compared with those who employ the older methods; for how can he determine the hardness or density of minerals with accuracy of

their lustre and colour, or recognise their crystalline character, and their behaviour with chemical reagents? In face of these objections every effort has been made to increase the delicacy and accuracy of optical methods of examination.

Anyone who would have an idea of the results obtained by the means described, when employed by experienced and skilful observers, need only look through the records of petrography for the last fifteen years; as a matter of fact these results have brought about a complete revolution in the science. On the other hand, anyone who has been occupied in the microscopic examination of minerals in thin plates, will be well aware, by his own experience, how much care and experience are required in order to achieve results worthy of confidence, and in how many cases, in spite of the most scrupulous care, there still remain doubts and uncertainties, especially when one is dealing with an old or much abraded specimen.

The use of apparatus for polarisation in the determination of the system of crystallisation, is only practicable in cases when the direction of cleavage, or the well-defined character of the crystal, renders the rotation of the principal axis possible. Sometimes it takes a considerable time to ascertain this, and in the case of amorphous matters or crystals of the regular system the above named method is entirely inapplicable. In fact, in the latter case one is obliged to depend on the differences of structure, transparency, and colour, and in more favourable cases on the character of the accompanying matter. As an example of these undecipherable bodies I may mention the fundamental matter of the different porphyry rocks, and the efflorescent products of felspar and augite, which have been named *saussurite* and *viridite*; and again, those opaque bodies, indefinite with regard to their crystalline form, which have been named *opacite* when of a black colour and *ferrite* when the colour tends towards brown; two names which have no advantage except in enabling us to say in one word that we do not know the true nature of the objects referred to.

(To be continued.)

ON CALCIUM BORATE.

By BERTRAM BLOUNT.

THE constant formation of definite vitreous balls, when caustic lime is taken up on a boric oxide bead before the blowpipe, which float insoluble in the surrounding medium, observed by Ross, led me to endeavour to prepare the body on a scale which would admit of subsequent analysis.

Accordingly freshly calcined lime was added to recently fused boric oxide in a platinum crucible, and the mixture heated over a Bunsen burner till the lime sank in and adhered to the boric oxide, so that none could be blown out when further heated in a Fletcher's gas-furnace.

In this apparatus perfect fusion was maintained for ten or fifteen minutes, the crucible removed while hot, and allowed to cool on an anvil, so as to thoroughly crack its contents.

While in a state of fusion the borate could be seen as a spheroid immersed in the pool of boric oxide, but when taken out cold it formed a layer, having its upper surface slightly concave, at the bottom of the crucible, and had no spheroidal shape.

The borate thus obtained was a hard glassy body, which cracked on cooling after fusion,—though less readily than boric oxide,—permanent in air, but slowly, though completely, decomposed by digestion with water.

Its composition was ascertained—

(i.) By synthesis.

(ii.) By analysis.

(i.) A weighed portion of lime, containing only small quantities of water and carbon dioxide as impurities, was

heated in a gas muffle till its weight was constant; boric oxide was then added, and the fusion conducted in the manner described above.

(In some cases pure dry calcium carbonate was used to start with: in this case it was first heated to expel the greater part of the CO_2 , to prevent frothing, and then treated with boric oxide.)

The crucible with its contents was then digested with warm methylated alcohol, and the insoluble borate received on a weighed filter-paper, washed with alcohol till free from boric acid, dried, and weighed. Alcohol, even when somewhat dilute, seemed not to affect the borate like water.

The numbers for one such operation are—

	Grms.
Weight of calcium carbonate taken ..	=1.2317
Weight of calcium borate obtained ..	=2.4546
\therefore Percentage of calcium oxide in the borate	=28.10 %.

(ii.) A weighed portion of the borate thus formed was dissolved in warm hydrochloric acid, diluted with an equal bulk of water, ammonia in excess added,—which brought down a white flocculent precipitate, probably some other calcium borate, acetic acid in excess added to re-dissolve this precipitate, and finally the lime thrown down by ammonium oxalate.

The calcium oxalate thus formed was either received on a weighed filter, or, if the weight of the filter was not known, it was removed from it and weighed separately, the filter being ignited over the blowpipe, and the particles adhering to it calculated as caustic lime.

This latter method is to be recommended for quickness without sacrifice of accuracy.

The weight thus obtained was confirmed by afterwards weighing the precipitate as any or all of calcium carbonate, oxide, or sulphate.

The numbers for such an analysis are appended:—

	Grms.
Weight of calcium borate taken	=1.45
Weight of calcium oxalate obtained ..	=1.0501
Weight of calcium oxide + filter ash ..	=0.0106
Weight of ash	=0.0003
\therefore Weight of calcium oxide	=0.0103
\therefore Percentage of calcium oxide in the borate	=28.49 %.

These numbers correspond more nearly to the composition of the calcium analogue of borax than any other compound.

Percentage of CaO in CaB_4O_7 :—

Calculated.	Found.
—	28.1 (synthesis)
28.57	28.49 (analysis).

This body is sufficiently well known, though the only mention I find of it is that it is obtained in the crystalline form by the fusion of various calcium borates, made by wet methods, with excess of boric acid in presence of a mixture of alkaline chlorides as a medium. (I observed the formation of such a substance when lime and excess of boric oxide are fused for some time in presence of alkaline chlorides, but did not analyse it.)

The salt is also found native, crystalline and hydrated, in Peru.

There were indications of the possibility of the formation of borates containing a higher proportion of boric oxide, if it were present in very large excess and the temperature were high.

This is quite compatible with the known tendency of boric oxide to combine with varying proportions of bases according to external conditions; as an instance one may note the expulsion by boric oxide, from excess of barium carbonate, of 2 or $2\frac{1}{2}$ molecules of carbon dioxide, according to the temperature employed (Bloxam). Accord-

ingly it is possible that the body obtained on a platinum-wire ring before the blowpipe, where the excess of boric oxide is very large and the temperature extremely high, may contain a larger proportion of boric oxide than that formed in a crucible in a gas-furnace; the preparation of a large number of globules before the blowpipe, and their analysis, is necessary for the confirmation or disproof of this supposition.

Chemical Laboratory, King's College,
September 20, 1886.

THE ACTION OF REAGENTS ON COBRA-POISON.

By C. J. H. WARDEN, Surgeon, H M.'s Bengal Staff,
Professor of Chemistry, Calcutta Medical College.

(Concluded from p. 199.)

In the experiments already quoted, it will have been observed that the duration of life after injection of the poison is inversely proportional to the dose administered. In the two experiments in which 0.00002 grm. was injected the mice lived for 1 h. 50 m. and 1 h. 17 m. respectively. With a dose between 0.00001 and 0.00002 grm. death did not ensue until over three hours after the injection. The maximum duration of life, therefore, after the administration of the minimum fatal dose, appears to be a period varying between three and four hours. Dealing with larger doses, it would appear that amounts varying between 0.0001 and 0.0004 of a gramme prove fatal in from 33 to 36 minutes. In order to ascertain the minimum duration of life after the injection of an overwhelmingly large dose, the following experiment was performed:—

Exp. 4.—0.02 grm. of dry but not anhydrous venom was dissolved in 0.5 of a cubic centimetre of distilled water. A full-grown mouse was injected at 11.13 a.m. with 0.3 c.c. of the solution; breathing ceased at 11.17 a.m. Ratio of poison to body weight, 1 to 1247. The animal was powerfully convulsed. A dose, therefore, of 0.012 grm. was fatal in four minutes.

Regarding the ratio of the minimum fatal dose to the body weight, it would appear that a ratio of 1 to 7,900,000 is fatal, but this is evidently not the extreme limit, as it represents the action of two-hundredths of a milligramme of dry but not anhydrous venom, while, as has been previously stated, there is reason to believe that the minimum fatal dose is more than one-hundredth, and less than two-hundredths, of a milligramme, equivalent to 0.000008 and 0.000016 of a gramme of the anhydrous poison. It may therefore be stated approximately that the maximum fatal ratio is probably one to ten or eleven millions. It need scarcely be pointed out that the fatal ratio of poison to body weight deduced from these experiments probably holds good only in the case of healthy full-grown white mice; and to draw any conclusions from these data as to the fatal dose to body weight in the case of other animals, would in all likelihood be fallacious.

The Action of Heat.—Wall was the first, I believe, who investigated with any precision the effect of heat on cobra-venom, and, as his results are of considerable interest, I thought it necessary to perform experiments on this point. But the effects of heat on cobra-poison possess additional interest, on account of the marked analogy which exists in the action of this physical agent on a poison of vegetable origin—*Abrus precatorius*—and which has been pointed out also bears a marked physiological analogy to snake-poison.

Exp. 5.—A solution of dry, but not anhydrous, cobra-poison, containing 0.0001 grm. per cubic centimetre of distilled water, was heated in a sealed flask in a water-oven for four hours. The highest temperature registered in the oven being 93° C. After heating, as the solutio

was somewhat milky, it was filtered, and with the clear filtrate four mice were injected.

- (a) With 0.2 c.c. Not fatal.
- (b) With 0.2 c.c. Not fatal.
- (c) With 0.4 c.c. Not fatal.
- (d) With 0.4 c.c. Not fatal.

In this experiment, thus twice the minimum fatal dose failed to kill.

Exp. 6.—A solution of dry cobra-poison was made, by dissolving 0.05 gm. in 50 c.c. of distilled water, and placed in a flask provided with a well-fitting cork carrying a thermometer, and the flask immersed in water, which was then gradually heated till the thermometer in the flask indicated 50° C., and this degree of heat was steadily maintained for three hours and twenty minutes. A portion of the liquid was then removed, and diluted in the proportion of 2 c.c. to 8 c.c. with distilled water. One mouse was injected with 0.1 c.c., equal to 0.00002 gm. of dry venom. Death ensued in one hour and twelve minutes.

Exp. 7.—The remainder of the undiluted solutions used in the last experiment was again heated to 65° C. for three hours and thirty-five minutes. A portion was then filtered and diluted with distilled water in the proportion of 2 to 8. With this diluted solution two mice were injected.

(a) With 0.1 c.c., equal to 0.00002 gm. Fatal in 3 hours 22 minutes.

(b) With 0.3 c.c., equal to 0.00006 gm. Fatal in 45 minutes.

Exp. 8.—The remainder of the undiluted solution from the last experiment was again heated to 75°–79° C. for three hours and fifteen minutes. As the solution was only faintly opalescent it was not filtered. A portion was diluted to the same strength as employed in the last two experiments. Two mice injected.

(a) With 0.1 c.c., equal to 0.00002 gm. Not fatal.

(b) With 0.3 c.c., equal to 0.00006 gm. Death in 55 minutes.

Exp. 9.—The remainder of the undiluted solution from the last experiment was once more heated to 85° C. for four hours and fifteen minutes. The solution was now highly opalescent, and filtration through several folds of filter-paper failed to render it bright; a portion was therefore strongly agitated with a few small fragments of well-washed filter paper, and, by returning the filtrate two or three times, a bright transparent liquid was ultimately obtained. Two sets of experiments were now made, one with the unfiltered and turbid solution, and the second with the filtered and transparent.

Exp. A.—With unfiltered solution. Two cubic-centimetres diluted with 8 c.c. of distilled water. One mouse injected with 0.3 c.c., equal to 0.00006 gm. Not fatal.

Exp. B.—With clear filtered solution. Two cubic-centimetres diluted with 8 c.c. of distilled water. One mouse injected with 0.3 c.c., equal to 0.00006 gm. Not fatal.

Exp. C.—One mouse was injected with 0.2 c.c. of the unfiltered and undiluted solution equal to 0.0002 gm. Not fatal.

The results obtained by the foregoing experiments may be tabulated as follows:—

An aqueous solution of cobra-venom containing 0.001 gm. per cubic centimetre of dry but not anhydrous poison, when

Heated to 50° C. for 3 h. 20 m.—0.00002 gm. of the venom was fatal in 1 h. 12 m.

Heated to 60° C. for 3 h. 35 m.—0.00002 gm. of the venom was fatal in 3 h. 35 m. (0.00006 gm. in 45 m.)

Heated to 75°–79° C. for 3 h. 15 m.—0.00002 gm. Not fatal.

Heated to 75°–79° C. for 3 h. 15 m.—0.00006 gm. Fatal in 55 m.

Heated to 85° C. for 4 h. 15 m.—0.00006 gm. Not fatal.

Heated to 85° C. for 4 h. 15 m.—0.0002 gm. Not fatal.

The temperature at which a diminution in the toxic power of the venom is first strikingly apparent is between 79° and 85° C., and this range of temperature corresponds with the degree of heat at which a considerable precipitate occurs when an aqueous solution of the venom is heated. Experiment 5 indicated that after exposing a solution to 93° C. for four hours, that twice the ordinary fatal dose was inactive; in the subsequent experiments after 14 h. 25 m., non-continuous exposure of the same solution to temperatures varying between 50° and 85° C., ten times the minimum fatal dose failed to kill. The question here arose, is *time* a factor? In other words, in order to lessen the activity of the poison, is it merely necessary to heat a solution to a temperature of 85° C. for a few moments, or must that degree of heat be maintained for some time; and will exposure to a high temperature for a short period be equivalent to prolonged heating at a lower temperature? Again, as has already been pointed out, at 79°–85° C. there is a marked coagulation of albuminous matter; is the action of heat on this principle merely a physical one, or does it modify in any manner the toxic power of the venom considered as a whole? If the diminution in activity of the venom by heat be solely dependent on coagulation, then reagents which coagulate proteids ought to have a similar effect in lessening the activity of the poison. On the other hand, we have Mitchell's experiments, which indicate apparently the complex nature of the venom; it is therefore possible that the mere act of coagulation by heat, or by a reagent, may modify the toxic power of one constituent, without lessening in any marked degree the toxic power of the venom when considered as a whole. As bearing on these several points the following experiments were performed:—

Exp. 10.—An aqueous solution of cobra-poison containing 0.002 gm. of dry venom per cubic centimetre, was heated to 85° C. for five minutes. As only a small amount of solution was employed, the requisite temperature was reached in less than two minutes. An abundant precipitate was produced; the solution was allowed to cool, and a mouse injected with 0.2 c.c. of the unfiltered solution, equal to 0.0002 gm. of venom. Death ensued in 31 minutes.

Exp. 11.—To a solution of cobra-poison of the same strength as that employed in the last experiment, a small amount of solid picric acid was added, the liquid well agitated, and with the turbid solution one mouse injected with 0.2 c.c., equal to 0.0002 gm. Death ensued in 31 minutes.

Exp. 12.—As a control experiment a mouse was injected with the same amount of venom solution employed in the last two experiments, but without the addition of picric acid. Death ensued in 23 minutes.

Experiments 10 and 11 were performed at the same time, so that one control experiment sufficed. In these three last-quoted experiments the symptoms noted are worthy of record. In the case of the mouse injected with the solution which had been previously heated, after the injection it remained in one place in a crouching posture; the breathing at first was hurried, then became slower; the animal never moved, it seemed petrified; and it died in the same posture which it first assumed, without any convulsive movements whatever. In the case of the mouse injected with the solution containing picric acid, marked convulsive movements ensued prior to death. Without a control experiment it might be argued that Mitchell's "venom-peptone"—a convulsive agent—had been destroyed by the action of heat. The control mouse, however, which had received the same amount of poison, without having been previously heated, exhibited precisely similar symptoms; it never moved after the injection; it died in a crouching posture, and there was a total absence of convulsive movements.

It is interesting to note how the symptoms vary with

the dose of poison administered; thus with overwhelmingly large doses powerful convulsive movements ensue; doses approaching the minimum fatal limit also cause convulsions, but with a dose approximating to two-tenths of a milligramme of dry but not anhydrous poison, there is a total absence of all convulsive movements. These experiments indicate the caution with which inferences should be drawn of a change in chemical composition, when based merely on differences of physiological action.

Exp. 13.—A solution of cobra-poison containing 0.001 gm. per cubic centimetre of dry but not anhydrous venom was heated to 85° C. for five minutes, rapidly cooled and filtered. The clear filtrate gave a slight precipitate with picric acid, another portion on further heating became slightly opalescent. One mouse was injected with 0.1 c.c., equal to 0.0001 gm. Died in 35 minutes with marked convulsions.

Exp. 14.—A fresh solution of the same strength as used in the last experiment was heated in a water-bath to 85° C., which occupied six minutes, and the solution was kept at that temperature for five minutes, and then rapidly cooled. One mouse was injected with 0.2 c.c. of the unfiltered solution, equal to 0.0002 gm. of dry but not anhydrous venom. Death ensued in twenty minutes; no convulsive movements.

Exp. 15.—The solution used in the last experiment was again heated to 85° C., which occupied four minutes, and then kept at that temperature for ten minutes. Total heating below a temperature of 85° C. ten minutes, and at 85° C. fifteen minutes. After heating the solution was rapidly cooled, and a portion filtered; 0.2 c.c. of the filtrate injected into a mouse caused death in thirty minutes, with a total absence of all convulsive movements.

Exp. 16.—The remainder of the unfiltered solution from the last experiment was again heated to 85° C., which occupied six minutes, and then kept at that temperature for fifteen minutes and rapidly cooled. Total heating below 85° C. sixteen minutes, at 85° C. thirty minutes. One mouse injected with 0.2 c.c. of the unfiltered solution. Death in thirty-nine minutes; no convulsive movements.

Exp. 17.—A fresh solution was prepared, containing 0.001 gm. of dry venom per cubic centimetre of distilled water; and the solution heated continuously to 85° C. for forty minutes and allowed to cool slowly. One mouse injected with 0.2 cubic centimetre of the unfiltered solution, equal to 0.0002 gm. of venom. Death in thirty-six minutes.

Exp. 18.—A fresh solution of venom was prepared, of the same strength as that used in the last experiment, and rapidly boiled for two minutes. One mouse injected with 0.1 c.c., equal to 0.0001 gm. Death in thirty-five minutes.

Exp. 19.—Solid picric acid was added to a solution of venom containing 0.001 gm. per cubic centimetre, the solution well agitated and immediately filtered. The filtrate was yellowish, from excess of picric acid, but perfectly bright. On heating a small portion no cloudiness ensued. One mouse was injected with 0.2 c.c. of the unheated filtrate; the animal was decidedly affected, but death did not ensue. The remainder of solution was kept, and after standing for 62 hours at 15° C., yielded a considerable white precipitate, and to the presence of this coagulable matter the symptoms which followed the injection were probably due.

The experiments which have been described would appear to indicate that the mere act of coagulation by heat at 85° C., or at 100° C. of certain principles contained in an aqueous solution of cobra-poison does not lessen in any marked degree the toxic power of the venom. Similar remarks would also appear to apply to a reagent such as picric acid, which causes an abundant precipitate in solutions of the poison. With heat as the coagulating agent, coagulation is probably the first visible step in the chemical change in constitution of one or more of the

proteids which go to make up the venom. For heat to lessen the toxic power of cobra-poison, time is a most important factor; short exposure to a high temperature not being equivalent to the prolonged action of a lower degree of heat.

The Action of Picric Acid.—A solution of cobra-venom containing 0.0002 gm. per cubic centimetre of distilled water was mixed with an excess of solid picric acid, the mixture was agitated and immediately filtered. One mouse was injected with 0.1 c.c., equal to 0.00002 gm. of dry but not anhydrous venom. Not fatal, though the symptoms produced were marked.

As a control experiment one mouse was injected with the same amount of cobra-venom solution, without the addition of picric acid. Death ensued in twenty-seven minutes, being immediately preceded by violent convulsions.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To COLONEL SIR FRANCIS BOLTON, *Water Examiner,*
Metropolis Water Act, 1871.

London, October 7th, 1886.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be perfectly clear, bright, and well filtered.

Altogether the character of the London water supply has continued to be excellent throughout the past month. The mean proportion of organic carbon in the Thames-derived supply was 0.133 part, with a maximum in any one sample of 0.151 part in 100,000 parts of the water, as against a mean of 0.141 part, and a maximum of 0.177 part in the preceding three months' supply.

The succeeding paragraphs set forth the general results of a third series of bacteriological experiments, made in continuation of those described in our two previous monthly reports. In these experiments Thames-derived ordinary town-supply water was sterilised during the passage through it of a current of sterilised carbonic acid, so as to retain the earthy carbonates in solution. After sterilisation it was allowed to become re-aërated by standing for forty-eight hours in cotton-plugged flasks before being subjected to experiment. In each experiment, by means of sterilised pipette-bulbs as nearly as might be of equal capacity, a quantity of peptone-fluid, loaded with an active sporeless growth of *bacillus anthracis*, was added to the sterilised water in the proportion, roughly, of 1-600th or 1-700th of its bulk; though it is possible

that this proportion may, now and then, have been more or less departed from. To contaminate to the same extent the entire daily flow of Thames water from which the daily London supply is withdrawn, would require an addition thereto of over a million gallons of bacillus-charged animal fluid; while to contaminate to the same extent a day's supply of the Thames water actually withdrawn would require an addition thereto of at least a hundred thousand gallons of the same animal fluid. The experiments were made mostly on different days from May 4 to May 19, inclusive. In twelve duplicate experiments the infected water was kept at the temperature of the room, which ranged from 58° to 63° F. (14.5 to 17.5° C.); while in four single experiments it was maintained artificially at the temperature of 90° F. (32° C.). After intervals of half an hour, and again after intervals of six hours, tubes of sterilised culture fluid were sown with the infected water, and subjected to incubation for eighteen hours and longer at 90° F. (32° C.). The general result of this series of experiments is as follows:—

The tubes of culture-fluid, sown with the infected water within half an hour of its having been infected, were found invariably to exhibit, after eighteen hours incubation, a characteristic growth of bacillus. As regards the sowings made with the same infected water that had afterwards been kept for six hours at the temperature of the room, in one of the twenty-four tubes of culture-fluid, corresponding to the twelve duplicate experiments, there was some growth of bacillus observable after its incubation for eighteen hours; but subsequent sowings with this particular specimen of infected water, made the next morning, proved wholly infertile on incubation, though kept up for a period of three days. In the other twenty-three tubes of culture fluid, sown with water that had been infected six hours previously and kept at the temperature of the room, there was no development whatever of bacillus after an incubation extending in each experiment to three, and in some instances to four days. Similarly, with regard to the four experiments in which the culture fluid was sown with water that had been infected for six hours, during which it was maintained at the temperature of 90° F., in no instance did the sowings prove fertile on even prolonged incubation.

Subsequent series of experiments were undertaken with a view to ascertain whether the duration of the period of infectivity in purposely infected river water in its ordinary state differed at all from that observed in the case of the sterilised river water; and also to ascertain the influence of a greater or less proportion of added nutrient animal fluid in prolonging or diminishing the duration of the period of infectivity. Particulars of these series of experiments will be given in future reports.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

CORRESPONDENCE.

CONDENSATION OF GASES BY POROUS BODIES.

To the Editor of the Chemical News.

SIR,—The interesting paper by the Rev. A. Irving, on Dissociation and Contact-Action (CHEMICAL NEWS, vol. liv., p. 179), recalls a speculation which occupied my mind a good deal three or four years ago, as to the cause of the condensation of gases by porous bodies: the two subjects, though not identical, are closely related, and an adequate explanation of one is likely at least to throw light upon the other.

If we start with a vessel of ordinary proportions containing a gas, and suppose the diameter to be gradually narrowed, we see that an increasing number of molecular shocks must fall upon the rigid walls instead of expending themselves upon neighbouring molecules. In the theory put forward by Mr. Irving the greater violence of this impact against a solid is supposed to be transformed into intra-molecular energy tending to dissociation, but there are further consequences involved into which he does not enter. If the walls of the containing vessel be narrowed until it becomes a pore not greater than the mean free path of the molecule, it would seem as if the motion of the latter would consist to a great extent of a violent rebound from wall to wall, leaving the space behind it comparatively free from pressure, and therefore adapted for the close approach of another molecule in its rear; we should thus expect on *à priori* grounds that any minutely porous body would effect the condensation of gases.

Now it is probable that the clean surface of any metallic plate produced by pressure (such as blows or rolling) is minutely porous, but only those metals called "noble" are able to retain their cleanliness; the atmospheric oxygen enters the pores, is condensed in them, and thus brought into intimate molecular contact with their walls, owing to the violent rebounds required by the theory: this in itself would promote combination, independently of the transformation of energy postulated by Mr. Irving, which probably assists the reaction; and so we get a superficial oxidation and a plugging of the pores with oxide, which prevents further action.

The best illustration of the action of a porous body in condensing a gas is afforded by the familiar lecture experiment of introducing a piece of recently ignited charcoal into a tube containing ammoniacal gas over mercury, when the enormous force with which condensation is effected is shown by the mercury rising to the height of 10 or 12 inches in the tube.

A communication was prepared some time ago on the above subject, but was suppressed, partly because the ideas involved appeared crude and undeveloped, and partly on account of the great difficulty experienced, perhaps for that reason, in giving them clear expression. I am encouraged, however, by the appearance of Mr. Irving's paper to lay my views, which to some extent run parallel with his, before your readers.—I am, &c.,

THOS. BLUNT, M.A. Oxon, F.C.S.

The Wyle Cop, Shrewsbury,
October 15, 1886.

FLAME SPECTRA.

To the Editor of the Chemical News.

SIR,—Many of your readers may have found a difficulty, in common with myself, in procuring a continuous spectrum in the usual way, with a bead on platinum wire, in the Bunsen flame. Lately I have used a solution of the salt, injecting it as spray into the flame by means of an ordinary glass spray producer attached to a pair of Fletcher's bellows, with complete success. Others may perhaps be glad to know this, and to improve upon my simple method. And the manufacturers of chemical apparatus may think it worth while to give us a lamp suited for use with the spectroscop on this principle.—I am, &c.,

G. F. M. FIELDING.

Hobart, September 1, 1886.

Formation of Sulphuric Acid during the Preparation of Dithionic Acid.—W. Spring and E. Bourgeois. The facts observed demonstrate that SO₂ forms with water a very instable compound, which is oxidised by manganese peroxide to the state of dithionic acid; SO₂ not hydrated, though dissolved, passes into the state of sulphuric acid.—*Bull. de la Soc. Chim. de Paris.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 13, September 27, 1886.

Researches on Sugars.—M. Berthelot.—The author has recently investigated some new principles resulting from the mutual association of the sugars, not in stable combinations like the saccharoses, but compounds easily split up, even by solvents, and similar to the hydrates and alcoholates. He obtained a compound of levulose and glucose, characterised by its rotatory power, found to be $\alpha_D = +32.2^\circ$.

No. 14, October 4, 1886.

On Sodium Glycerinate.—M. de Forcrand.—Glycerin is attacked in the cold by the alkaline metals, with formation of a glycerinate and escape of hydrogen. The reaction is soon arrested in consequence of the viscosity of the liquid, the fragments of the metal being coated with a layer of solid glycerinate. If heat is applied the matter turns black and an explosion ensues. In 1872 Letts published a process for preparing sodium glycerinate by precipitating sodium ethylate dissolved in an excess of absolute alcohol by an equivalent quantity of glycerin. It is a very general property of the alkaline glycerinates to unite with a molecule of a mono-atomic alcohol to form crystalline compounds; the author has obtained several of these compounds analogous to the poly-alcoholic ethylates and methylates. From a table here given it appears that the quantities of heat evolved increase progressively; the polyatomic alcohols give compounds more stable than do the monoatomic alcohols, and from this point of view they are intermediate between the latter and the aldehyds or the phenols.

Preparation of Calcium Sulphide having a Violet Phosphorescence.—A. Verneuil.—There exists in commerce a calcium sulphide remarkable for the intensity and duration of its violet phosphorescence. The analysis of this product shows that it is composed of calcium monosulphide about 37 per cent, lime 50 per cent, calcium sulphate 7, and calcium carbonate 5 per cent, with traces of silica, magnesia, phosphates, and alkalies. The presence of tests of siliceous foraminifera shows that the lime employed has been obtained from the shells of a mollusk. On further examination he detected a very small quantity some ten thousandth parts, of bismuth sulphide. The following method for its preparation gave the best results:—20 grms. lime obtained by igniting the shell of *Hypopus vulgaris* to bright redness are finely pulverised and intimately mixed with 6 grms. roll sulphur and 2 grms. starch. To this mixture are added, drop by drop, 8 c.c. of a solution containing $\frac{1}{2}$ gm. bismuth subnitrate, 100 c.c. absolute alcohol, and a few drops of hydrochloric acid. When the chief part of the alcohol has evaporated, which will require about half an hour, it is heated for about 20 minutes to a light cherry red heat in a covered crucible. When completely cold the slender layer of gypsum which has been formed on the surface is removed, the product is pounded and ignited again at the same heat for fifteen minutes. If the heat has not been too strong the product obtained is formed of small grains scarcely agglomerated. A repeated pulverisation diminishes the phosphorescence. Pure calcium sulphide does not phosphoresce for any appreciable length of time. The substances which render the sulphide phosphorescent are those which frit slightly under the influence of heat.

Comparative Volatility of Methylic Compounds in the Various Families of the Negative Elements.—Louis Henry.—For equal atomic weights the decrease of volatility effected in methane by the substitution of a

negative element X for hydrogen is so much the greater as this element is more negative, and consequently more remote from hydrogen.

Bulletin de la Société Chimique de Paris.

Vol. xlv., No. 2, July 20, 1886.

At the Session of the Society, June 25, 1886, M. Maumené mentioned the fact that potash alum dried, not over sulphuric acid but over calcined alum, contains 29 equivalents of water, a fact foreseen by his general theory. M. Maumené also laid before the Society the details of the industrial preparation of vermilion, which he obtains by causing mercury to react upon calcium sulphide. He obtains at pleasure either the black modification by using a dilute solution containing a little ammonium hydro-sulphate or the scarlet variety by heating the mixture to about 110° .

Reaction for Distinguishing Coal-Tar Colours from Colouring Matters of Vegetable Origin.—Ch. Blarez and G. Deniges.—The author's researches bear upon the detection of colouring matters in wines. They take 10 c.c. of the wine under examination, add 10 drops of glacial acetic acid, and heat to 100° . They then throw into the hot liquid 0.20 grm. of pulverised mercuric acetate, cool under a jet of cold water, and pour upon a filter. All the natural wines examined have been decolourised or have given a feebly yellowish filtrate. It has proved the same with wines coloured with vegetable dyes. Wines coloured with the majority of coal-tar products give a coloured filtrate.

Contribution to the Study of the Platinum Salts.—Eug. Prost.—At present we generally consider as normal salts those which result from the union of molecules of anhydrides and bases in a simple proportion according to their valency. This view seems scarcely admissible; it implies, in fact, that a molecule of a given anhydride is saturated to the same degree on uniting with a molecule of any oxide whatever, strong or feeble, and conversely, that any molecule of base exhausts its chemical energy by combining with a molecule of the different anhydrides. According to this conception sulphuric anhydride would be equally saturated by a molecule of the oxide of potassium, of zinc, or of lead. In fact the matter is scarcely rational. We may ask if the molecules of oxides which enter into the composition of the so-called basic salts are not there to supply a want of energy in the base as compared with the anhydride? Are not the salts now known as basic rather to be regarded as normal? The author proposes to contribute to the verification of this fact by studying the combinations of platinum oxide, one of the feeblest bases, with the various strong anhydrides. He has accordingly examined platinum nitrate, perchlorate, sulphate, and the double salts of platinum and of the alkaline metals. The facts ascertained show the insufficiency of the chemical energy of platinum oxide with regard to the strong anhydrides.

Justus Liebig's Annalen der Chemie,

Vol. ccxxxiv., Parts 1 and 2.

Researches on the Molecular Refraction of Liquid Organic Bodies of Great Power of Dispersing Colours.—J. W. Bruehl.—The dispersion of colours effected by different bodies bears so far no distinct relation either to the refraction of light which they exercise or to the chemical nature of the substances. The constant $(n-1)\frac{P}{d}$, hitherto used as an expression for molecular refraction, is generally applicable only for bodies of the fatty series, but for unsaturated compounds it is serviceable only in cases of feeble dispersion, and even then its results are not always trustworthy. If the dispersion is strong it is quite. For examination of the relation between

luminous refractive power and constitution the above formula is therefore to be rejected and the value—

$$\frac{(n^2 + 1) P}{(n^2 + 2) d}$$

is to be used in its place.

Non-Acid Components of Bees'-Wax.—Fr. Schwalb.

Action of Aluminium Chloride.—R. Anschütz.—The first portion of a very extensive memoir which does not admit of useful abstraction.

Supplementary Remarks on Pseudo-morphine.—O. Hesse.—The author criticises the researches of Polstorff and Donath on this subject, and gives his views on the origin of pseudo-morphine from morphine.

MISCELLANEOUS.

Evening University Lectures at King's College, London.—During the winter, commencing on October 25th, five courses of lectures, having similar scope to those delivered at the Universities, and given with a view to assisting independent study, will be given at King's College. Each course will consist of not fewer than eight lectures, the subjects being, French and German Literature, Classic History and Art, the Geometry of

Newton, and Iron and Steel. In the last-named course, which will be delivered on Tuesday evenings from 7 to 8, it is proposed to treat of the general methods by which the different qualities of malleable iron, cast iron, and steel may be produced and prepared for use in the Arts; of the effect of the various foreign substances contained in these metals upon their strength and fitness for the purposes to which they are to be applied; of the extent to which these substances are injurious, and the means by which they are commonly eliminated.

Poisonous Properties of the Hop.—Hopeine, a principle found most abundantly in the wild hops of America, produces effects very similar to those of morphine, but acts more powerfully if introduced subcutaneously. It is found as a white powder, sparingly soluble in water, but dissolving very readily in 40 parts of absolute alcohol. Its composition is $C_{18}H_{20}NO_4 + H_2O$. If placed on the tongue it occasions a burning sensation, which masks for the moment the decided bitterness. In a small dose it produces sleep, but in larger quantities it occasions coma and death by paralysis. The ingestion of 0.05 grm. brings on symptoms of poisoning; 0.1 grm. is a dangerous dose for a man, and quantities of 0.1 to 0.05 grm. prove fatal to dogs, cats, &c., in about four hours. Hopeine is a powerful antiseptic, and arrests fermentation. It is hoped that it may prove of service in the treatment of zymotic diseases.—*Dingler's Journal*.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1405.

ON THE NATURE OF SOLUTION.*

By SPENCER UMFREVILLE PICKERING, M.A.,
Professor of Chemistry at Bedford College.

THE "hydrate" theory attributes dissolution to the existence, in a stable or partially dissociated condition, of definite liquid compounds (generally unknown in the solid form) of the substance dissolved and its solvent, and the mixing of these compounds with excess of the solvent.

In certain special instances we have direct evidence of the reality of such compounds,† but it is on general grounds rather than on any special experiments that I would seek to establish their existence.

There is, in the first place, a strong *prima facie* improbability that substances such as copper sulphate, potassium hydrate, &c., which possess such an intense affinity for water, should be capable of existing in the anhydrous condition in the presence of an unlimited amount of water.

We know, moreover, that in a great number of cases—where a dehydrated salt is placed in water—hydration does undeniably precede dissolution,‡ and in such cases the salt can only exist in the liquid in the uncombined state if the continued action of the solvent is to decompose the hydrate which it has just formed. The only two forces by which such a decomposition might be supposed to be effected are (1) the attraction of the bulk of the water present for the few molecules of water combined with the salt; (2) the attraction of this same bulk of water for the (anhydrous) salt molecules. On the one hand, however, it is absurd to imagine that the mass of water molecules possess such a strong attraction for the few contained in the hydrate as to decompose this latter, or, even if they did, that they would ever have given them up to the salt in the first instance; and, on the other hand, it is equally absurd to urge the intensity of the attraction of the salt molecules for the water molecules as a reason for these two parting company.

Another general fact, which lends considerable support to the view that the dissolution of a salt is due to the formation of a hydrate, is, that those salts which combine with water always *dissolve* in that liquid, and, as a rule, the greater the energy with which they do combine with it, the greater is their solubility.

The thermal phenomena attending the act of dissolution point incontestably to the same conclusion. When a dehydrated salt (say MgSO_4) is dissolved in water a considerable evolution of heat occurs; and by the simplest experiment it can be established, beyond any possibility of doubt, that all, or the greater portion of this heat is due to the hydration of the salt. If the salt be taken in the hydrated condition less heat is evolved, and, without a single known exception, this evolution diminishes continuously as the salt taken is more and

more highly hydrated; but even when taken in its most highly hydrated condition the evolution of heat is in many cases still very considerable.* Now unless we can reconcile ourselves to attribute the heat evolution in this latter case to a cause entirely different from that which exists in the other cases,—unless we are content to shut our eyes to the proportionality between the heat evolved and the degree of hydration of the salt taken,—we must admit that even with a fully hydrated solid salt the heat evolved is due to further hydration; that not only do hydrates exist in solution, but that they are often of a higher order than the highest known in the solid condition.

Coming now to the other side of the question, we find many general considerations, as well as special results, brought forward against the hydrate theory of solution. The latter, however, are for the most part, I consider, urged on mistaken notions, and prove nothing *pro* or *con*.

Thus Dr. Nicol's study of the molecular volumes of salts in solution shows that their volumes are entirely uninfluenced by the presence or absence of water of crystallisation in the solid salt; that if any water is still combined with the salt when dissolved it acts in the same way, and is quite indistinguishable from the rest of the solvent present. In so far as his conclusion that these molecular volumes afford no evidence in support of the existence of combined water, I entirely agree with Dr. Nicol; but in concluding that therefore no water is combined, he has pushed his conclusions far beyond legitimate limits. The same reasoning that leads to the belief that the water and the salt bear no chemical relationship towards each other in solution would hold equally good with reference to the radicles of which the salts themselves are constituted, as Favre and Valson indicated in 1875 (*Comptes Rendus*, lxxv., 1000). Each radicle possesses its own specific volume entirely uninfluenced by the nature of the other radicle with which it is combined: the radicles behave independently, and as if there were no combination between them.

Nor is it only from a study of the volumes of salts in the dissolved state that such results are obtained. Numerous determinations of the extent to which the vapour-pressure, the freezing-point, and the temperature of maximum density of water is influenced by the presence of various salts in it, have been made by Wüllner, Blagden, Dufour, Depretz, Rüdorff, and De Coppet,† with the general results that certain hydrates of the salt are in some cases present and in others the salt is anhydrous; but these conclusions, which would tell more against the hydrate theory than for it, are eminently unsatisfactory. The whole question, however, has been reopened by Raoult (*Ann. Chim. Phys.*, (5), 28, 133; (6) 2, 66, 4, 401); and by an exhaustive extension of the work, and by including solvents other than water, and solids other than salts, he has thrown a new light on the subject. Not only does the salt, in its influence on the freezing-point, show no signs of the presence of combined water, but it shows no signs of itself being a single compound; each of the radicles contained in it acts independently of the other, and in precisely the same manner as a *molecule* of a non-saline substance (see especially *loc cit.*, 4, 426). Precisely similar conclusions as to the apparent non-combined state of radicles in a dissolved salt were arrived at by Valson in his work on capillarity (*ibid.*, 1870) and by Hugo and Vrié (*ibid.*, 1883) in their examination of the effect of membranes on salt solutions. Other instances of a similar nature, physical and thermo-chemical, might be quoted.

That atoms or molecules which are undoubtedly united may retain their individuality so far as to act towards

* Discussion on the "Nature of Solution." British Association, Birmingham Meeting, Section B.

† See especially Bertholot, *Ann. Chim. Phys.* (5), 4, 445 to 537.

‡ Dr. Nicol (*Phil. Mag.*, 1885, i., 453, and ii., 295) quotes experiments with sodium sulphate in opposition to this view. He shows that the dehydrated salt may dissolve in water under certain circumstances without any signs of previous hydration. When it does so, however, it forms a supersaturated solution, which is certainly very different from a normal solution, being, according to Dr. Nicol's determination of the solubility, due to the extension at lower temperatures of conditions which exist naturally only above 33°: but when it dissolves to form a *normal* solution it is with evident signs of hydration. Whatever this may prove as to the supersaturated solution, it certainly does not prove that the normal solution contains the anhydrous salt,—rather the opposite.

* Thus the "true" heat of dissolution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is +7000 cal., and even this number is probably 1000 to 3000 cal. too low, as it contains no allowance for the heat of fusion of the MgSO_4 molecule. (See *Chem. Soc. Trans.*, 1886, 279.)

† For a general summary and discussion of the results from the point of view of these physicists, see De Coppet, *Ann. Chim. Phys.* (4), 23, 366; 25, 502; and 26, 98.

certain agents as if they were free, is surely not surprising; and from such methods as would lead us to conclude that the very radicles composing a salt are uncombined, it would be useless to look for evidence of the more feeble combination of the salt with its water, and inconsistent to argue, from the absence of such evidence, that no combined water is present.

Although I am not inclined to attribute any weight to these special experiments brought forward against the hydrate theory, it is otherwise with more general considerations.

The formation of hydrates cannot explain the absorption of heat which in many cases accompanies dissolution. The phenomena of solution are too universal to permit of imagining the existence of some definite compound of the dissolved substance with the solvent in every case. There is a continuous influence exerted by the salt on its solvent too extensive to be accounted for by the effect of mass on partially dissociated hydrates; there is a continuity between the fused and dissolved states in many cases, and a regularity in the variation of solubility with change of temperature, &c., which cannot be thoroughly explained on the hydrate theory.

However undeniable the existence of these compounds may be in many cases, they do not give an adequate explanation of all the facts of dissolution.

The hydrate theory can be neither rejected nor accepted.

The explanation of this contradiction is not, I think, very difficult to find. We are talking about molecules of solids and liquids, not as they exist, but as they do *not* exist. Our chemical formulæ for them represent but the results of analysis, or, at the most, the constitution of the substance in that transitory state of simplification which immediately precedes entire decomposition; what their composition may be when in the free state, and removed from all decomposing forces, we know not: all we do know or believe about them is, that they are then far more complex than chemical formulæ represent.

Crystalline form alone would show that a number, probably a very great number, of our so-called molecules combine together, bear certain definite relations and hold certain definite positions towards each other, producing a molecular aggregate or physical unit, which alone should receive the name of molecule.*

Just as a number of similar particles unite to form an aggregate or true molecule of any simple substance, so will dissimilar particles unite to form aggregates of a more complex nature.

It is but natural that our prejudices in favour of the "laws" of chemical combination and atomic valency, to which we owe so much, should lead us to attribute the variable composition of certain substances to our imperfect means of investigation rather than to the non-conformity of these substances to our laws. Whether we be right or not in our explanation, we must acknowledge that apparent *inconstancy* in composition is one of the most marked features of immense classes of substances which cannot be termed other than chemical compounds.

The varied composition of minerals is said to receive an explanation in the statement that isomorphous substances may displace each other in definite proportions, but to an indefinite extent. This is undoubtedly true, but it does not obviate the necessity of recognising the existence of some form of attraction between these isomorphous substances. No purely mechanical or physical cause can explain this phenomenon; mere similarity of crystalline form has been proved to be incompetent to

produce such results. A selective power is exhibited by the substances which thus unite,* as well defined as that selective power which in the case of simpler substances has received the name of chemical affinity, and the resulting compounds are characterised by the same uniformity in composition and physical properties† which is the attribute of acknowledged chemical compounds.

Nor is it with minerals and artificial crystals only where we find ourselves in what would appear to be a wide border-land between chemical compounds and mixtures. Whether we study the formation of alloys, the occlusion of gases by solids, ranging from the most mechanical action by insensible graduations to the formation of a substance having every appearance of a definite compound, or the decomposition of some of the firmest chemical bodies by so-called mechanical means (filtration), or the constant change in composition of many basic salts with change in the circumstances of their formation—we are forced to admit that the definiteness which characterises the combination of atoms may be absent from, or at any rate unrecognisable in, the combination of our so-called molecules to form complex aggregates.

When we examine the constituents of these apparently indefinite compounds, it becomes clear that it is only substances which resemble each other which can combine in this manner; and one of the most striking features of dissolution offers such a strict parallel to this, that its meaning can scarcely be mistaken.

A certain degree of similarity in nature between the solvent and the substance dissolved is the invariable accompaniment of dissolution.

Dissolution, I believe, is but one of the many results of apparently indefinite chemical combination.

We cannot obtain a satisfactory explanation of the composition of minerals by admitting the existence of *definite* double salts only, nor can we explain the phenomena of dissolution by confining our attention to *definite* hydrates only. These may, and in all probability do, exist in solution, but they are only small circles within the larger ones; their successive formation and decomposition would give rise to irregularities and effects such as those which are observed in some cases; but these irregularities would form but ripples on the more regular changes which would accompany the variations in the molecular aggregates,—variations which, as in the case of minerals, would be so dependent on physical conditions as to obliterate their chemical nature when examined from many points of view.

The evolution of heat accompanying dissolution will still be attributable, as on the ordinary hydrate theory, to the formation of chemical compounds, but the far greater complexity, and, consequently, instability of these, than of atomic hydrates, if I may so call them, will remove all difficulty in comprehending the continuous effect of the mass of the solvent upon them, even when the latter exceeds that of the salt many hundred fold; where heat is evolved, therefore, the evolution will be increased, though at a diminishing rate, by dilution.

The rapid increase in the heat of dissolution, produced by a rise of temperature, is but a necessary consequence of the formation of a chemical compound possessing a specific heat less than the sum of those of its components, and would of itself go far to prove that a solution did in reality contain such a compound. But a rise of temperature would also undoubtedly have another and opposing effect, for, being inimical to the complexity of these hydrates, they would be more dissociated at higher than at lower temperatures, and hence the heat of dissolution would not be so great as it should be according to the

* In a Paper read before this Section last year (Report, p. 989), I argued that our formulæ adequately represented the molecules of solids and liquids with which chemical reactions deal, although I fully recognised the existence of far more complex aggregates: my opinions have so far altered that at present I consider these aggregates to be recognisable in many operations which must be termed chemical, although in the great bulk of ordinary reactions the simpler or ultimate molecules need alone be considered.

* A power or "affinity" so strong that it will sometimes induce a salt to separate out in a crystalline form and with a proportion of water foreign to its nature, as well as from a solution too weak to yield it of its own accord (Aston and Pickering, "Multiple Sulphates," *Chem. Soc. Trans.*, 1886).

† J. M. Thomson, on the "Double Sulphates of Nickel and Cobalt" (*Brit. Assoc. Rep.*, 1877, 209).

various specific heats. This is precisely what Dr. Tilden has proved to be the case (*Proc. Roy. Soc.*, 1885, 401).

There is, however, another action which I believe accompanies every act of dissolution resulting in the *absorption* of heat.

The heat absorbed by a large number of salts in dissolving can not be freely accounted for by the mere physical change of the solid into the liquid salt. Thus, the heat of dissolution of potassium nitrate is -8500 cal., and that of sodium nitrate -5000 cal., whereas the heat of fusion of these salts at the same temperature is but -1300 and -2300 cal., respectively. There must be some other heat-absorbing action besides the fusion of the salt. The amount of heat thus absorbed increases also with the dilution of the liquid. Moreover, we cannot, I think, account for the manner in which heat is evolved in one case and absorbed in another, or the way in which an absorption of heat sometimes gives place to an evolution, as the temperature or other conditions are changed, but by admitting the constant coexistence of two actions producing opposite thermal effects, and being influenced to different extents by an alteration of circumstances.*

On the theory which I am here advocating this absorption of heat receives a ready explanation. Whatever be the complexity of the molecular aggregates of a liquid, those of a solid will be still more complex. Fusion would, therefore, entail their simplification; it would be but a chemical decomposition absorbing heat; this simplification would be pushed much further, however, when the salt is dissolved instead of being merely fused, for the particles of the liquid act chemically (*ex hyp.*) on those of the solid and combine with them themselves; the cold absorbed on dissolution would exceed that absorbed on fusion, and would, moreover, be increased by increasing the amount of the solvent. This accords fully with the facts observed.

All the phenomena attending dissolution are, therefore, I contend, accounted for by a full recognition of the real complexity of the units of matter, and by taking the more liberal view of chemical combination which is inculcated by a study of minerals and other substances. Every act of dissolution involves two actions. The chemical decomposition of the more complex aggregates of the solid into a simpler form, absorbing heat, and a chemical combination of these with the liquid, evolving heat; the only quantity which we can at present measure is the algebraic sum of these two.

Mr. DURHAM next gave a short statement of his own theory of solution:—

When, for example, common salt (NaCl) is placed in water, all the atoms act upon each other. The sodium of the salt acts upon the oxygen of the water, and the chlorine of the salt upon the hydrogen of the water; and the result is a definite compound, which we call a solution. The heat of formation of the acid is neutralised by the heat of formation of the oxide. If they be not equal, the difference is the heat of the solution; if they be equal, the heat is of course *nil*. If the former be the greater, the heat of the solution is negative; if the latter, it is positive. Solution arises from chemical affinity, and takes place inversely as the attraction between the positive element and the oxygen—and the negative element and the hydrogen—of water. But chemical affinity is itself physical; the atoms are physical, and all forces which act upon them must be physical forces. In a chemical mixture every atom is acting upon every other atom, but such action can be nothing else than physical; and we are therefore led to the conclusion that there is really no difference between chemical and physical action, and,

consequently, that the alternative between the two does not exist.

In the course of the "Discussion on the Nature of Solution," and preceding the reading of Mr. Pickering's paper, the following remarks were made:—

Dr. ARMSTRONG said that, from the summary given by Prof. Tilden, it appeared that the two important questions for discussion were—(1) Does water of crystallisation exist in solution combined with the salt as it did prior to dissolution? and (2), What distinction is to be drawn between chemical combination and mechanical association or adhesion? In short, are the phenomena of dissolution of a chemical or of a mechanical character? But Prof. Tilden had made an important omission, inasmuch as he had not discussed the possible simplification of the molecules on dissolution: in discussing the evidence afforded by the various phenomena, everything turned upon the question whether the crystal molecules are of the composition represented by our ordinary formulæ, or are more or less complex.

As regards the first question, Prof. Tilden appeared to differ from Dr. Nicol, and to think that water of crystallisation did exist in solution. (Prof. TILDEN, interposing, desired to explain that what he had said was that it was impossible, in the case of any solution, to say that one portion of the water is in combination with the salt and that another is not; all the phenomena of dissolution and dilution being continuous, no point can be found at which such a distinction can be set up. He believed that the salt was attached to all the water present without exception.)

Dr. ARMSTRONG, resuming, said that much of the evidence appeared, he thought, to favour the conclusion that in certain cases water of crystallisation did exist in solution; *e.g.*, the difference in colour between many hydrated and dehydrated salts taken in conjunction with the colour of their solutions. Again, many dehydrated salts dissolved much less readily than the corresponding hydrated salts: instances of this kind were not common among inorganic salts, but were often met with among organic salts, and the speaker cited calcium butyrate and certain naphthalene- and naphthol-sulphonates as examples. Dextrose, again, ordinarily crystallises with two molecules of water, but if dehydrated and carefully dissolved in water at a low temperature it may be crystallised out from the solution in the anhydrous state. T. Thomsen's recent experiments, however, appeared to show that when two substances were dissolved in water they appropriated the water in the proportions in which they were present, thus favouring a purely mechanical interpretation of the phenomena of dissolution; but, on the other hand, it was to be noted that in the case of citric and sulphuric acids, for example, Thomsen's results were in accord with this conclusion only when it was assumed that the citric acid was present as the dihydrate and sulphuric acid as the monohydrate, $\text{H}_2\text{SO}_4 \cdot \text{OH}_2$. In fine, the speaker was of opinion that while the question could not be regarded as settled, yet there was a considerable amount of evidence that the water was not evenly distributed, but was, in some cases at least, in part directly combined with the dissolved substance. Dr. Nicol had deduced an ingenious argument from J. Thomsen's observations on heats of neutralisation. As a criticism of Dr. Nicol's argument from the existence of neutralisation constants he would venture to say "Put not your faith in constants." If the views which he held—views which probably were at present peculiar to himself—were correct, the quantities in question ought to have a constant value. According to Helmholtz, all atoms hold a positive or negative electrical charge, a single charge being associated with a monad, two with a dyad, and so on. If when combination takes place these charges exactly neutralised each other, all compounds would be neutral and saturated; but actually this is not the case: in point of fact, there is no such thing as a saturated compound.

* A study of the thermal results attending the dilution of salt solutions, established by Thomsen ("Thermochem.," iii., especially plate iv., and also the curves given by formic and acetic acids and by potassium and sodium hydrates), impresses very forcibly the coexistence of these two actions, although Thomsen himself does not seem to have noticed it.

Helmholtz seems to think that the charges may be held by different atoms with different degrees of force, but the speaker took a somewhat different view, and thought that probably when two atoms combined, in consequence perhaps of peculiarities of structure, their charges were not completely used up; the resulting molecules therefore possessed a certain residual charge or affinity, and were consequently in a position to enter into combination with other molecules. Thus water, he thought, was not a saturated compound; its oxygen atom was still possessed of residual affinity. The same was true of sulphuric acid. Consequently the two could combine together to form a hydrate. On neutralising a dilute solution of alkali by a dilute solution of acid, a stable condition is finally attained, and it is to be assumed that the affinities are fully satisfied, or very nearly so—that the charges practically neutralise each other: hence it may be expected that the heat of neutralisation will have nearly a constant value provided there be no disturbance such as the separation of a precipitate would produce. But the value of each of the several processes which go to make up the heat of neutralisation are entirely unknown to us, and in the absence of such knowledge it is impossible to place much confidence in arguments based upon the study of such complex phenomena.

As regards the question of chemical *versus* mechanical action, the speaker could only imagine one form of mechanical action attending dissolution, viz., that of the water molecules bombarding the surfaces of the solid, and as it were chipping off particles. All other actions, in so far as they could be regarded as involving the attraction of the molecules of the dissolved substance by those of the solvent, he was inclined to class as chemical. Nothing was more certain than that dissolution depended both on the nature of the solvent and of the substance dissolved. Like dissolves like—water is *the* solvent for bodies containing oxygen; sulphur compounds are dissolved by carbon bisulphide; phosphorus compounds by chloride of phosphorus; shale spirit, which is rich in olefines, and especially rosin spirit, which is rich in acetylenes and benzenes, were far better solvents of hydrocarbons and resinous bodies than petroleum, which consisted of saturated inert hydrocarbons, and was the worst of solvents. Facts such as these spoke strongly in favour of the conclusion that the phenomena of dissolution are largely of a chemical character.

Prof. W. N. HARTLEY was understood to base the argument in favour of the hydration theory chiefly on the changes of colour observed in the solution of certain salts in various proportions of water. The chlorides, bromides, and iodides of cobalt, nickel, and copper exhibit these phenomena most plainly. Thus the iodide of cobalt in the anhydrous state is black, its dihydrate is green, the hexhydrate a reddish brown. If this last be dissolved in water a pink solution is formed, which probably contains a richer hydrate. The brown saturated solution of the hexhydrate is a very dense liquid, of specific gravity about 3, and when water is added to it the formation of the pink liquid is attended by a large evolution of heat, and this affords evidence that the hydrate exists in the solution. Again, hydrated cupric chloride contains two molecules of water, and when quite dry is of a pale blue colour. Its solution in water has the same colour unless it be heated, and then it turns green. Nickel salts behave similarly. So that the evidence, on the whole, warrants the belief that when a hydrated salt is dissolved in water the water of crystallisation remains a constituent part of the molecule.

Dr. GLADSTONE commenced his remarks by a discussion of the question, What is a salt in solution? Is the solution of a salt in water a process analogous in any degree to the decomposition which takes place when one salt is mixed with another? Take, for instance, chloride of sodium and water. Many years ago the speaker had endeavoured to determine whether any chemical decomposition of the salt by the water occurred so as to give rise

to sodium hydrate and hydrochloric acid, but he had come to the conclusion that this decomposition took place, if at all, only to a very small extent. Many salts, as had already been stated, combine with water to form coloured hydrates, and the hydrate is of a colour different from that of the anhydrous salt. But a coloured hydrate, when dissolved in a sufficient quantity of water, is never changed by further dilution. The speaker had endeavoured to ascertain whether the specific refraction of substances was altered by solution. He had found that no alteration could be detected, and this result was afterwards confirmed by the experiments of other chemists. The refraction equivalent of a solution is equal to the sum of the refraction equivalents of the salt and the water present. In an alum solution, the water of crystallisation supposed to be in combination with the salt is not distinguishable by its refractive power from the water of solution outside it. It seems impossible, however, to arrive at a conclusion with regard to the constituents of a solution. The idea of reciprocal decomposition is not supported by experimental evidence, save in some exceptional cases, and the actual condition of a dissolved salt seems beyond expression by formulæ.

A NEW PROCESS FOR THE PRODUCTION OF THE ALKALI METALS.*

By HAMILTON Y. CASTNER, of New York.

I SHALL first proceed to give a brief description of the process heretofore employed for manufacturing the alkali metals, together with the defects of the same, which prevent an economical production of metal, before explaining the method I have invented for their reduction, and its advantages over the older process. Although in the following paper mention is only made of sodium, the same remarks are intended to apply to potassium, the process being practically alike in the production of either metal. The method formerly used consists in igniting, at an intense heat, an intimate mixture of nine parts of sodium carbonate, four parts of charcoal, and one part of lime in wrought-iron vessels, cylindrical in form, placed horizontally in a furnace, the said cylinders being furnished with a small tube to conduct the metallic vapours and gases produced during the reduction, into the attached condenser, wherein the vapours are condensed and the sodium obtained. The cylinders must be constructed of wrought-iron, this being the only metal possible to use that will stand the heat, and the dimensions of the same must not exceed a diameter of six inches or a length of five feet. The mixture of sodium carbonate, charcoal, and lime must be finely ground and calcined, to render it more compact, previous to placing it in the cylinders. Lime is added to make the mass refractory, otherwise the alkali would fuse when the charge is highly heated, and separate from the light infusible carbon. The carbon must be in the proportion to the sodium carbonate as four is to nine, which is found needful in practice, so as to assure each particle of soda in the refractory charge having an excess of carbon directly adjacent or in actual contact. Notwithstanding the well-known fact that sodium is reduced from its oxides at a degree of heat but slightly exceeding the reducing point of zinc-oxide, the heat necessary to accomplish reduction by this process and to obtain even one-third the metal contained in each charge, closely approaches the melting-point of wrought-iron. Any process devised for the manufacture of sodium, by which its cost could be reduced, would have to be an improvement over the older method in one or more of the following directions, namely:—

(1.) The process should be more simple in its details,

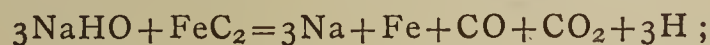
* A Paper read before the Chemical Section of the Franklin Institute, October 12th, 1886.

and not require the care and management necessary in carrying on the process or method now used.

(2.) Performing the reduction at a comparatively low temperature and so save in the fuel and prevent the excessive destruction of iron, which at present stands for one-half the cost of the sodium produced.

(3.) By increasing the yield of sodium, as in the old process, when one-third the metal contained in the charges is obtained, the result is considered very satisfactory.

The process which I employ consists in reducing either the hydrate or carbonate of an alkali, when in a fused state, at moderate temperatures, by the use of the carbide of a metal or its equivalent, whereby an excess of carbon is avoided and the use of lime is rendered unnecessary. The reducing substance, due to its composition and gravity, remains below the surface, and is therefore in direct contact with the fused alkali. By the equivalent of the carbide of a metal, I mean a mechanical compound of carbon and metal from which the metal cannot be separated, excepting by the aid of acids or intense heat. Such a compound I produce by coking a mixture of tar and iron (previously reduced in a fine state of division by carbonic oxide or hydrogen). From experience such proportions of tar and iron are used as will produce, when the mixture is coked, a heavy mass of metallic coke, having about the composition of, iron 70 per cent and carbon 30 per cent, equivalent to the formula FeC_2 . This mechanical compound, after being ground, is ready for use, and consists of fine particles of iron, coated with carbon, fully answering the purposes of a true carbide. I prefer to use caustic soda in the preparation of sodium, on account of its fusibility, and with it mix such quantity of the so-called "carbide" that the carbon contained in the mixture shall not be in excess of the amount theoretically required to reduce all the soda to sodium, according to the following reaction:—



or, to every 100 pounds of pure caustic soda, fifteen pounds of "carbide," containing about twenty-two pounds of carbon, is added. The treatment of this mixture is carried on in large cast-iron crucibles, in a furnace, the general arrangements of which are as follows:—The heating space of the furnace is divided into separate chambers, the dimensions of the same depending upon the size of the crucibles to be heated, and the number of these compartments are in proportion to the capacity of production desired for the furnace. An aperture is provided in the bottom of each chamber, through which the crucible may be raised by mechanical means into its position in the furnace. The necessary cover for the crucible is fixed stationary in each chamber, and from this cover projects the tube to the outside of the furnace into the receptacle for the condensation of the metallic vapours. When operating the crucibles are charged with the mixture, made as before described, placed upon the lift, which is situated directly below the aperture made in the bottom of the chamber, and raised into the furnace. The edges of the covers are made convex, while the edges of the crucibles are concave, so that when the crucibles are raised the edges come together, and, being held from below, form a tight joint, preventing the exit of gas and vapour, excepting through the tube provided from the cover. Gas, which is used as a fuel in connection with heated air, is allowed to enter the chamber after the crucible containing the charge is in place, and the reduction and distillation commences as soon as the crucible contents have reached the temperature of 1000°C. , the sodium being reduced in the crucible and distilled therefrom into the condenser by passing through the tube projecting from the crucible cover. As soon as the operation is finished, the crucible is lowered and a new one containing a fresh charge is raised in its place, while the crucible just removed is cooled, cleaned and recharged. The appliances which hold the cover in

place are so arranged that the cover may be removed whenever necessary without interrupting the process, which is practically continuous. By avoiding the careful mixing and calcining of ingredients, preparatory to charging the cylinders, and in carrying out generally the mechanical part of the old process, the details of which require the most careful management, the method just described will be seen to have many advantages. As the charge is fused, the alkali and reducing material are in direct contact, and this fact, together with the aid rendered the carbon by the fine iron, in withdrawing the oxygen from the soda, fully explains the chemical reasons why the reduction is accomplished at a moderate temperature. Furthermore, by reducing the metal from a fused mass, in which the reducing agent remains in suspension, the operation can be carried on in crucibles of large diameter, the reduction taking place at the edges of the mass, where the heat is greatest and the charge flowing thereto from the centre to take the place of that reduced. By the old process, the heat required to penetrate to the centre of the refractory charge, and reduce the soda there situated, in addition to the heat absolutely needful to bring about reduction, necessitates the use of wrought-iron vessels, and even when these are made small in diameter, which partially removes this great disadvantage of the method, the expensive cylinders are rapidly rendered worthless from the effects of the intense heat.

In doing away with the use of lime and an excess of carbon, the main causes which have hitherto prevented a full yield of metal are removed, and thus, with the aid of other advantages described, I am enabled to obtain fully 90 per cent of metal, instead of 30 per cent as formerly. By the old process lime must be added, to prevent fusion, to insure any reduction, yet at the same time it forms, with a portion of the soda, the compound known as soda-lime, and from this substance carbon reduces sodium only at the most intense heat. In practice, according to the old method, four pounds of carbon are used to every nine pounds of sodium carbonate. This is twice the amount theoretically required to reduce all the sodium, even assuming the gas resulting from the reduction to be wholly carbonic oxide. When, however, but one-third the total amount of sodium is all that is obtained from a charge, the proportion between the sodium produced and carbon used becomes as one is to six. The effect of an excess of carbon in the mixture, which, as previously explained, is really necessary, is to produce an excessive amount of carbonic oxide, and this, together with the excess of carbon, combines with the metallic vapours of sodium, forming various compounds, from which the metal cannot be distilled. By reducing caustic soda with the carbide of a metal, or its equivalent, and using only sufficient carbon to carry out the reaction stated above, the gases given off consist of hydrogen, carbonic oxide, and carbonic acid, which mixture has little or no effect upon the vapours of sodium. The crucibles, after treatment, contain a small amount of carbonate of soda and all the iron of the "carbide" still in a fine state of division, together with a very small percentage of carbon. These residues in the crucibles are treated with warm water, and the solution of soda evaporated to recover the carbonate of soda, while the fine iron is dried, mixed with tar, and coked to produce more of the so-called "carbide equivalent."

The Composition of Urine after the Internal Use of Oil of Santal.—C. Mehu.—After the internal use of the essential oil of santal there is found in the urine a resinous matter of santal-like odour, and it appears to be held in solution by sodium phosphate, which plays the part of a weak acid. The oil of santal, if pure, does not impart to the urine a smell of violets.—*Journal de Pharmacie et de Chemie.*

ON THE
MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 208.)

2. *Micro-Chemical Methods.*

WE have often felt inclined to turn for help to chemistry, which, in the hands of Klaproth, Berzelius, Rammelsberg, and others, has been of such immense service in the determination and classification of minerals, and we should doubtless at the present time possess a complete system of micro-chemical methods of determining the more common minerals if they were as easily attacked by chemical reagents as even the most refractory organic tissues are. The morphological reagents (acetic acid for the interior of the cells, and potash for the envelopes) are of no use in the examination of minerals, on account of not being able to soak in.

The application of methods based on colouration can only be of very limited use, inasmuch as there are but few minerals which have the property of absorbing colouring-matters, and above all of fixing them. Maceration with acids and saline solutions seems to promise better results, but up to the present this method has been so little used that it is impossible to make it the basis of a rational system of analysis.

The treatment of minerals by means of hydrochloric acid, of which we have already made mention (1), may be considered as resulting from this general method. As a rule we take some of the powdered mineral to effect this, but the results are not easy to decipher. It is, in fact, only necessary to remember the numerous cases where this process, because of the confusion of microscopic images, has led to contradictory statements as to the nature of the substance, and has given rise to serious doubts as to the value of the method. Let us further remark that hydrochloric acid applied in the ordinary manner, that is to say, in an aqueous solution more or less concentrated, to very thin plates, often leads to the total destruction of the material under examination.

From what has preceded we draw this conclusion, that we cannot arrive at a positive result by this method without entirely destroying a certain portion of the silicates, either by acting on a restricted portion of the polished surface, or by attacking, by the reagent, a picked sample of the mineral, and applying the regular rules of qualitative analysis.

M. H. Rosenbusch, who has often made use of chemical reagents as auxiliaries, recommends, in his "Physiographie Microscopie" (vol. i., p. 108) the simultaneous application of the chemical and optical methods, and even gives (pp. 107 to 111) some instructions as to the micro-chemical manipulation, on which we can make successful use in divining the nature of minerals. The principle of his method, applied either to the powdered mineral or to thin plates of the substance, can be condensed as follows:—

1. Partial dissolution by acids or alkalies of the integral matter, and qualitative analysis of the substance dissolved according to recognised methods, availing oneself of the microscope when necessary.
2. Microscopic examination of the residue, immersed in Canadian balsam.

M. Rosenbusch's method necessitates the use of filters. The filtering apparatus described by him would no doubt serve to reduce, as much as possible, the loss of time in this kind of research, as well as the still more deplorable loss of material; but it must be admitted that it would be very desirable to substitute another method by which a qualitative analysis could be done without having recourse to filtration.

3. *M. Boricky's Method.*

M. E. Boricky has the merit of being the first who has published a rational system of micro-chemical reactions.

He tries in every case to do without filtration, and he uses but one principal reagent. It is this that gives a real advantage and an elegance to his method which reflects great credit on him.

M. Boricky based his "*universal method*" on the property of hydro-fluosilicic acid of being decomposed by evaporation and forming hydrofluoric acid, and giving, with alkalies, crystalline salts, very slightly soluble and of a very distinct form. He submits to evaporation hydro-fluosilicic acid at 3½ per cent, in contact with fragments of minerals, or with the polished surface of a stony material,* and he distinguishes the fluosilicates formed by means of their crystalline forms.†

The potassic salt forms cubical crystals; the sodic salt hexagonal prisms, crowned with a pyramid, with obtuse angles. The calcic salt is found in the form of rods, and the magnesian salt as rhombohedrons. The strontic compound resembles the calcic, while that of barium gives little pointed needles, and that of lithium small six-sided pyramids. The observations were made under a magnifying power of from 200 to 300 times.

To distinguish calcium from strontium M. Boricky uses sulphuric acid diluted with its own volume of water.‡ By this reagent the crystals of fluosilicate of calcium change into masses formed of crystals of gypsum, whilst the fluosilicate of strontium is transformed into a granular mass hardly recognisable.

Fluosilicate of sodium is not attacked by sulphuric acid. To distinguish between the fluosilicates of magnesium, iron, and manganese, they are treated either with chlorine or with sulphide of ammonium: under the influence of chlorine the ferrous salt takes a light yellow colour, and the manganese salt becomes of a reddish tint, while the sulphide mentioned colours the ferrous salt black, and precipitates from the solution of the manganous salt a greenish grey substance, having a granular appearance. It is well understood that the magnesian salt is unaffected by either of the above-mentioned reagents.§ As to the application of the other reactions indicated by the author (experiments with heat and the corrosion of polished plates), I must refer the reader to the original; only I will here take the opportunity of remarking that several of the phenomena attributed by the author to the action of chlorine might very possibly be caused by the action of hydrochloric acid vapours.

M. Boricky has proved, by several controlling experiments, that it is possible to obtain very good results by employing his method, and, as far as I am concerned, my own trials have confirmed this. If, however, in spite of this success, I have found it necessary to stray a little from the rule he lays down, it is because it contains some grave faults, which can only be found by practice, and that it is not always easy to apply.

It is this which caused me successively to examine the method more closely, to complete, and then to modify it. The experience which serves to show the presence of alkalies leaves little to desire as to manipulation, but much as to ease of carrying out.

The manner of carrying it out is simple; it is to let a drop of hydro-fluosilic acid dry on a polished plate of the mineral. In this experiment, white crusts are formed which are hardly transparent, and often do not allow us

* E. Boricky, *Elemente einer neuen Chemisch-mikroskopischen Mineral- und Gesteinsanalyse*, p. 15 and following, in the *Archiv der Naturwissenschaftlichen Landesdurchforschung von Böhmen*, Bd. 3, Abth. 5.

† *Ibid.*, p. 17 to 22.

‡ *Ibid.*, p. 22.

§ *Ibid.*, p. 23.

|| *Ibid.*, pp. 15, 16. The author asserts that the silicic acid separates in considerable quantities in a concentrated solution of hydro-fluosilicic acid. In this case he finds himself forced to have recourse to potash to dissolve the jelly, which is only partially successful, while the addition of concentrated sulphuric acid would give a satisfactory result. It results from this that the matter which is separated is not silicic acid, but we have to deal with the rapid formation of fluosilicates, and, in the greater number of cases, with the formation of fluoaluminates, difficult to decompose.

to distinguish the adjacent white crystals, notably those transparent ones of fluosilicate of potassium. We obtain much better results by drenching the little masses of mineral in drop of acid (p. 15), because then a part of the fluosilicates formed is shown distinctly on a colourless back-ground, quite transparent. I have always obtained the best crystals by boiling the fluosilicates in water, and placing several drops of the liquid on a plate of glass: this method is used by M. Boricky in his experiments with hydrofluoric acid (p. 31).

(To be continued).

SOME PROCEDURES OF QUALITATIVE ANALYSIS BASED UPON MICRO-CHEMICAL REACTIONS.

BORICKY made the first attempt to dispense with filtrations and to use only one principal reagent, hydrofluosilicic acid, which serves to distinguish the bases contained in a silicate. He spreads upon a glass slip a thin layer of Canada balsam, moderately dry, fixes in it by fusion a small fragment of the mineral, and places, upon it a drop of the acid. The action is allowed to go on in the cold for twenty-four hours in a moist place, and the preparation is then left for twenty-four hours longer, still in the cold, in dry air. The bases of the mineral pass into fluosilicates, which crystallise slowly and are examined with the microscope. Those of the magnesian series (magnesium, zinc, manganese, iron, nickel, cobalt, copper) all crystallise in hexagonal crystals and are respectively distinguished by their colour and their behaviour with ammonium sulphide. The process is especially applicable to potassium, sodium, and calcium. Potassium fluosilicate, a sparingly soluble salt, forms regular cubes or octohedra of remarkable limpidity, absolutely monorefringent. The corresponding sodium salt, more soluble, forms hexagonal prisms, sometimes bipyramidal, with a uniaxial double refraction, very slight and negative. The calcium salt is very soluble, crystallising in lamellæ, spindles, or oblique prisms with curvilinear outlines, strongly double refractory.

Th. Behrens has published a method for detecting a large number of elements in a fragment of a mineral less than $\frac{1}{2}$ m.grm. The portion, finely powdered, is attacked in a platinum crucible with a few drops of pure hydrofluoric acid or by ammonium hydrofluoride mixed with hydrochloric acid. He evaporates, re-dissolves in sulphuric acid to decompose the fluorides formed, evaporates again, and finally re-dissolves in water acidulated with sulphuric acid. This drop containing the sulphates is fractionated by means of a capillary pipette and serves for the various assays.

Calcium is recognised by the prisms and needles characteristic of gypsum being deposited as the drop evaporates.

Potassium.—To the drop is added platinic chloride, which gives the usual precipitate in small regular yellow octohedra.

Sodium (and Potassium).—The author uses a reagent, cerous sulphate, which gives crystalline precipitates with sodium and potassium; the former gives granules much finer and less soluble.

Lithium.—After removal of calcium in the state of gypsum the liquid mixed with sodium carbonate gives prisms of lithium carbonate with rectangular apices.

Barium and Strontium are found in the state of insoluble salts at the bottom of the platinum capsule along with excess of gypsum. They are soluble in boiling sulphuric acid. This solution on dilution and cooling deposits first barium sulphate in very small lenticular crystals laid crosswise, then strontium sulphate in crystals similar but much larger, and lastly gypsum.

Magnesium is detected as magnesium-ammonium phosphate.

Aluminium is recognised by the addition of a solution of caesium chloride, which yields regular octohedra of caesium-alum, very slightly soluble.

Sulphur.—The substance is converted, if needful, into a soluble sulphate, and chlorides of aluminium and caesium are added to form caesium-alum.

Phosphorus and Arsenic are converted, if needful, into soluble phosphate or arseniate, and the ammonium-magnesium phosphate or arseniate is produced. Arsenic is distinguished by heating the substance in a small tube with sodium carbonate and potassium nitrate.

Chlorine may be recognised by the addition of acid lead nitrate. If there is sulphuric acid in the liquid thallium sulphate is used instead, which precipitates thallium chloride in very small regular octohedra or rhomboidal dodecahedra, often in groups and presenting a remarkable refraction. Instead of searching for chlorine in the solution of the mineral it is preferable to distil the latter with sulphuric acid, placing a drop of cold water in contact with the vapours given off, which are thus condensed, and serve for the assays. Bromine acts like chlorine. We may also recognise chlorine by a mixture of platinum and potassium acetates, which give rise to the formation of the double chloride.

Fluorine.—The mineral (previously opened up, if necessary, with sodium carbonate and moistened with acetic acid) is heated with sulphuric acid, adding, if needful, silica or powdered glass. The vapours are condensed under a little platinum lid, moistened with a drop of dilute sulphuric acid. If fluorine is present it passes into the acid in the state of hydrofluosilicic acid. This is deposited upon a slip coated with Canada balsam, and sodium chloride is added. There are then formed rosettes, hexagonal tables, and bipyramidal prisms of sodium silicofluoride.

Boron and Silicon.—We proceed as for the detection of fluorine, but we distil with fluor-spar. The silicon and boron pass into the drops in the state of hydrofluosilicic and hydrofluoboric acids. We add to these drops, as above, sodium chloride, which yields a silicofluoride and a borofluoride, both crystallised in rosettes, tables, and hexagonal prisms. To decide between silicon and boron and to demonstrate the presence of both, if needful, we add potassium chloride, which yields the well-known silicofluoride (see Boricky's process, above) and a borofluoride in narrow plates with acute apices or rhombic crystals, much more soluble than the silicofluoride. If both boron and silicon are present it is well to fractionate the products of distillation, as boron fluoride is evolved only in the second place.

Water is found by heating the fragment in a glass tube with a drawn out point. The deposit is concentrated in the capillary part, and the reaction may be rendered more sensitive by the introduction of a tiny fragment of magenta, which, under the influence of moisture, loses its metallic lustre, giving a red transparent liquid.

M. Streng indicates a method of effecting micro-chemical filtrations and washings of precipitates, operating upon a few drops of liquid. He uses a band of filter-paper arranged on a glass slip slightly leaning; the drop to be filtered is placed at the upper end. He describes also the following micro-chemical reagents:—

Chlorine (and Silver).—Silver chloride is an amorphous precipitate, not characteristic under the microscope, but it becomes so if dissolved in ammonia and allowed to evaporate, when it is deposited in octohedra, cubes, or cubo-octohedra. It may further be heated in strong hydrochloric acid; on cooling silver chloride is deposited in octohedra.

Selenium.—Sulphurous acid is allowed to act upon the drop, when the selenium is thrown down in small opaque grains.

Phosphorus is converted into a soluble phosphate; silica, if present, is eliminated, and the phosphorus is recognised as ammonium phospho-molybdate.

Antimony is converted into a hydrochloric solution and there is added barium tartrate precipitate suspended in water. If antimony is present the liquid, on slow evaporation deposits rhombic crystals of antimony barium tartrate.

Sodium and Uranium.—On adding uranium acetate sodiferous solutions deposit uranium-sodium acetate in regular tetrahedra of a pale yellow. The uranium acetate used must be very pure. Inversely, uranium may be recognised by the use of a solution of sodium acetate.

Lithium.—The author uses sodium phosphate, which yields a precipitate of lithium phosphate in spindles and stellar groups.

Calcium, Strontium, Barium.—Oxalic acid produces in calcium solutions octohedra or rhombic tables; the two metals are distinguished by the action of sulphuric acid upon the crystals. There is nothing similar with barium. Barium solutions yield rhombic crystals with tartar emetic; those of strontia act similarly, but the crystals formed are less soluble. Barium tartrate forms rounded granules, whilst strontium and calcium yield crystals. Potassium ferrocyanide, added hot to a barium salt, form, on cooling, a deposit of barium and potassium ferrocyanide in pale yellow rhombohedra.

M. H. Rosenbusch in his "Microscopische Physiographie," mentions the following reactions:—

Barium chromate, formed by precipitation, quite resembles the crystallites of barium sulphate deposited in hot sulphuric acid.

Glucinum solutions, mixed with platinum chloride, yield, on slow evaporation, crystals of glucinum chloroplatinate in square or octagonal tables, almost colourless and optically negative uniaxial.

Chrome is converted into alkaline chromate, and a solution of silver nitrate is added. Silver dichromate is formed in rhombic tables, often truncated at the obtuse angles, of a hyacinth red and strongly refringent.

Cerium.—Oxalic acid or ammonium oxalate give a flocculent precipitate which crystallises spontaneously in fine needles highly double refractory. In heat there is a formation of rhomboidal tables.

Yttrium and Erbium are also recognised by means of oxalic acid and ammonium oxalate.

Titanium is attacked with potassium disulphate, and the mass is moistened with hydrogen peroxide. An orange-yellow colouration shows the presence of titanium.

Zirconium.—Attack with sodium carbonate at bright redness and dissolve in acidulated water. If zirconia is present it forms small hexagonal tablets.

Tungsten.—The substance is melted with nitre, dissolved in water, and calcium chloride is added. If tungsten is present cubes, square tablets, or bipyramidal prisms of calcium tungstate are formed.

Tantalum and Niobium.—The substance is fluxed with phosphorus salt, taken up in water, and caustic soda is added. There are formed colourless prisms of sodium tantalate or niobate, often grouped in tufts or stars.

Vanadium.—The substance is attacked with sodium carbonate and potassium nitrate, taken up in water, and a little ammonium chloride is added. There are formed navicular or cuneiform crystals of ammonium metavanadate, double refractive.—*Bulletin des Elèves de M. Fremy* (April, 1886, p. 145).

ANALYSES OF COMMERCIAL FERTILISERS.*

On Thursday, August 26, the Association assembled in the rooms of the Chemical Division of the Department of Agriculture at 10 o'clock, Dr. H. W. Wiley, the President, in the chair.

In calling the convention to order the President read the

following letter from the honourable Commissioner of Agriculture to the Executive Committee:

UNITED STATES DEPARTMENT OF AGRICULTURE.
Washington, D.C., August 7, 1886.

GENTLEMEN,—The results of your deliberations last year, as published in Bulletin No. 7, have proved of great advantage, not only to the chemists engaged in agricultural work throughout the country, but also to the farmers generally.

The existence of such an association as yours is a necessity, and I desire, in every way possible, to promote its efficiency. Permit me, therefore, to extend to you again an invitation to meet at the Department of Agriculture and to offer all the facilities in my power to make your approaching meeting agreeable and successful.

There are still many problems connected with agricultural chemical analysis which demand your serious attention. Permit me also to suggest that it would both be wise and profitable for you to extend the scope of your investigations to other subjects than those immediately connected with the analysis of fertilisers. It seems to me that there is no subject within the scope of agricultural chemical analysis which does not properly fall within the range of your discussions. I am anxious to see all the agricultural chemists in the country participating in your work and contributing to its efficiency.

I hope to be able, as last year, to aid in bringing the results of your deliberations prominently before the people, and promise you every assistance in my power to that end.

Again extending to you the courtesies of the Department, I am, respectfully,

NORMAN J. COLMAN,
Commissioner of Agriculture.

To the Executive Committee of the
Association of Official Agricultural Chemists.

Dr WILEY then addressed the convention as follows:—

GENTLEMEN,—For the second time under its present organisation our Association has met in Washington. It seems proper, in reviewing the work of our society during the past year, to congratulate you on its results. The proceedings of our last meeting, published through the courtesy of the Commissioner of Agriculture as a bulletin of the Division of Chemistry, have had a large circulation and have attracted much attention. It is gratifying to us to know that this bulletin was reproduced in full in the CHEMICAL NEWS, and received favourable mention in many other scientific journals. But it would be idle to think that the work so well begun is already perfect. A first step forward has certainly been taken, but the road before us is still a long one. Were it not so, the necessity of this and future meetings would not exist. But the success which has already attended our efforts has been great enough to warrant further exertion and give hope of greater achievements. It is evident to every one, however, that in our annual meetings, extending over a period of only a few days, little can be done except to bring together results and compare experiences. The patient and laborious work which alone can give a solid basis for the business of this association must be done in our laboratories and repeated until it gives a sufficient proof of its accuracy. Happily the methods adopted by our committees secure the accomplishment of this work in the most thorough manner, and I doubt whether any other such system of determining the value of any analytical methods is practised anywhere else in the world.

In looking over the means used in other countries to secure uniformity in the application of analytical methods, we may find many valuable indications to help us in the work which we have undertaken. In France we find an association of chemists devoted to the interests of sugar production and of the manufacture of alcohol. This association has adopted processes of analysis for the examination of fertilisers which they have recommended for use. Already two bulletins have been issued by this body, the second of which is a neat little pamphlet of 43 pages de-

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

voted to a discussion of the best methods of estimating phosphoric acid in fertilisers.

The treatment of the subject is in greater detail than the reports of the various Committees of this Association, which have had the subject in charge, but I doubt whether the practical results obtained have been any greater than those achieved by the labours of our own members, who have had this subject under special consideration. Since some of our number may not have seen the results reached by the French Committee, I will give a brief summary of them here. The Committee in charge of the work consisted of the following eminent agricultural chemists:—MM. Déhérain, Joulie, Aubin, and Dupont. Attention is first called to the importance of taking the sample; an importance which is fully recognised by this Association, but which perhaps has not been fully set forth. The French chemists recognise two kinds of samples, commercial and analytical. The commercial sample should be taken from various parts of as large a quantity of the fertiliser as is accessible, and by a person neither interested in the purchase nor sale of the substance. Then it is directed to proceed as follows:—

If it is fine powder, as ground phosphates in certain manures, it suffices to pass it two or three times through a sieve with very small meshes, 1 m.m. for example, being careful to grind the material each time in order to pulverise the fragments which the sieve may retain. Spread out the whole in a thin layer on a large sheet of paper and take here and there with a spatula small portions, which will give a quantity of 20 grms., from which is taken, afterwards, the sample to be assayed.

If the sample is in more or less large pieces like those of the rock phosphates, or coarsely pulverised like those of guanos containing conglomerated particles, it is necessary first to reduce it to powder by passing it through a mortar or through a small drug mill. Pass it then through a No. 60 sieve and grind again the remainder on the sieve until all passes entirely through. This point is very important, as the particles which resist the pestle frequently have a composition different from those which are broken up at first.

When the products for analysis contain organic materials, such as horn, meat, dried blood, &c., the grinding is often long and difficult, and produces a certain degree of heat which drives off the moisture in such a way that the pulverised product is finally drier and consequently richer than the original sample. It is important to note this desiccation, and as the pulverisation of a mass is not done without loss, the determination of the total weight of the sample before and after crushing does not give exact results.

It is, therefore, indispensable in this case to determine the moisture before and after the pulverisation and to restore by calculations the analytical results obtained in the pulverised samples to that which they would have had in the moist state of the original sample.

To avoid this necessity, as well as those difficulties which would thus result, owing to variations in the moisture during transportation, several chemists have thought that the best method of procedure would be to always dry the commercial product before submitting it to analysis, and to give in their reports their value in the dry state accompanied by the determinations of moisture, thus leaving to those interested the trouble of calculating the contents in the normal state, that is to say, the real state in which the merchandise is sold.

In addition to the fact that this method gives rise to numerous chances of error, much of the material undergoes important changes in composition by the mere fact of its drying. It has occasioned, in consequence, the worst frauds.

The retail dealers put these products on sale with a guarantee of their dry state, and a large number of farmers do not perceive the fraud which is hidden under this very innocent expression.

In this way guano containing 25 per cent of water has

been placed on sale as having 12 per cent of phosphoric acid, when in reality it had only 8 per cent.

Having thus secured as fair a sample as possible, it is recommended, inasmuch as the uranium method is to be used in the determination, to ignite it in order to destroy organic matter. In respect of the method of doing this the French chemists are silent, and it appears from this, as well as many other parts of the report, that they have not studied the publications of our society as carefully as they ought to have done.

The solution of the phosphate is a matter, however, to which they have given much attention, and on this point they make many valuable suggestions.

Solution of the Material.

All phosphates, with the exception of certain aluminum phosphates (amblygonite, for example), easily dissolve in nitric and hydrochloric acids, more or less dilute, especially at the boiling point. But the best solvent of calcium phosphates is, undoubtedly, hydrochloric acid, which also dissolves iron and aluminum phosphates which are often found in phosphate of lime.

Nitric Acid.

In many laboratories nitric acid is preferred, to avoid, as much as possible, the solution of the sesquioxide of iron, which interferes with the determination of phosphoric acid in certain methods of analysis.

Since this is not the case with the citro uranic method, it is preferable to employ hydrochloric acid, because it completely dissolves the iron, and thus permits one to judge of the completeness of the analysis by the perfect whiteness of the remainder.

Pyritical Phosphates.

Certain phosphates, as those of the Ardennes and of the Meuse, contain iron pyrites which hydrochloric acid does not dissolve, and consequently leaves a remainder more or less discoloured. It is thus necessary to add nitric acid in the beaker where the analysis is being made, and prolong the boiling until the pyrites has disappeared, otherwise it will retain a small quantity of phosphoric acid in the state of ferric phosphate.

Sulphuric Acid.

In Germany many chemists make the analysis of phosphates with dilute sulphuric acid. This method, which certainly gives good results for certain products, presents numerous objections which unfit it for general use. The calcium sulphate which is formed requires prolonged washing, which gives rise to many chances of error.

In the case of aluminum phosphate, containing little or no lime, sulphuric acid may be preferable to hydrochloric and nitric acids, for it attacks amblygonite, which resists the first two acids.

But one seldom meets with such a case, and can always make use of the general method by first fusing the material with the classic mixture of standard carbonate of soda and carbonate of potassium (containing, of course, no phosphate).

In the great majority of cases the solution with hydrochloric acid is made very easily by simply boiling in a beaker, and without affecting the separation of the silica.

This operation is only necessary after the use of alkaline carbonates, or for those substances which contain decomposed silica giving gelatinous silica during the action of the hydrochloric acid.

There are two ways of making the solutions of the sample, which weighs from 1 to 5, or even 10 grms., depending upon the apparent character of the material to be analysed.

Solution by Filtration and Washing.—One can work by the ordinary method, consisting of making the solution, filtering, washing the residue on the filter, and mixing the liquids, and making up to a definite volume, and then taking an aliquot part for precipitation.

This method is long, and occasions numerous errors when the insoluble remainder is somewhat voluminous and contains some silica, which fills up the pores of the paper and renders the filtration difficult.

Test for Arsenic Acid.—When the sample examined is pyritical it often contains arsenic.

Since this is acted on by nitric acid, it can produce arsenic acid. This behaves in all cases as phosphoric acid, and if it is found in the sample it will be precipitated and estimated with the phosphoric acid. It is sufficient, in order to avoid this cause of error, to pass first through the solution a current of sulphurous acid, to carry it then to the boiling-point to get rid of the acid, and finally to pass through it a current of hydrogen sulphide, which precipitates the arsenic. Immediately after filtration the series of operations described can be repeated.

Volumetric Solution.—We advise the substitution of volumetric solution for solution by filtration and washing. This consists in acting on the sample with the acid in a graduated flask, and completing the volume with distilled water. After cooling, filter without washing, and take, by means of a pipette, an aliquot part of the total volume to make the precipitation. Thus the delays and the chances of error of washing upon the filter are avoided. It is true that this method leads to a certain error, due to the volume of the insoluble material which is left; but, as this quantity of insoluble material is generally very small, and as it is always possible to diminish it by increasing the volume of the solution, this cause of error is much less to be feared than those which may be produced in the other method without the knowledge of the operator.

In this last recommendation we have almost the exact method recommended by our former Committees. Some objections have been urged against the method on account of the error due to insoluble matter; but this error, in the very nature of the case, is so small as to be negligible when compared with the errors and complexity of manipulation to which any other method of solution is liable.

The French chemists, while admitting the perfect accuracy of the phospho-molybdate method of estimating phosphoric acid, recommend solely the volumetric method first proposed by Joulie. The preliminary precipitation of the ammonio-magnesium phosphate is conducted as follows:—

A quantity of the solution representing about 0.25 gm. of the sample, or at most 1.0 gm., if the sample be poor in P_2O_5 , is taken. The total quantity of P_2O_5 in the sample taken should be about 50 m.grms. Then 10 c.c. of the citro-magnesian solution is added, and a large excess of ammonia. If the proper quantity of citro-magnesian solution has been used, the liquid will now remain perfectly clear.

The citro-magnesian solution should be prepared according to the following formula:—

	Grms.
Citric acid	400
Carbonate of magnesia (C. P.)	40
Caustic magnesia	20
Distilled water	500

After solution, enough ammonia (about 600 c.c.) is added to make the solution strongly alkaline, and the volume is then made up to 1500 c.c. If turbid the whole is to be filtered. After the magnesian phosphate is precipitated it should be allowed to stand at rest for some time (two hours) under cover, to avoid the evaporation of the ammonia. The filtration is made as carefully as possible, washing the precipitate with water containing one-tenth ammonia, and not bringing the precipitate on to the filter until near the last. The washing is continued (after all the precipitate is on the filter) until no precipitate is produced by phosphate of soda on the filtrate. The quantity of wash-water should be as small as possible. The phosphate is next dissolved in one-tenth pure nitric acid.

The beaker in which the precipitation was made should be rinsed with this acid. The filter-paper should finally be put into the flask receiving the solution. All having been collected in a 150 c.c. flask, marked also at 75 c.c., one-tenth ammonia is added until a slight permanent precipitate is formed. Two drops of one-tenth nitric acid are then added, and the flask placed on a sand-bath and raised to the boiling-point. Five c.c. acid acetate soda solution are then added, to neutralise the free nitrate acid. The acid acetate of soda solution is made as follows:—

	Grms.
Crystallised acetate of soda	100
Strongest acetic acid (glacial)	50
Distilled water, q. s., to make .. c.c.	1000

The solution of uranium is prepared according to the following formula:—

	Grms.
Pure nitrate of uranium	40
Distilled water	c.c. 800

Dissolve and add ammonia until a slight cloudiness is produced, and then acetic acid to clear the liquid. The volume is then made up to 1000 c.c. with distilled water.

To obtain perfectly pure uranium nitrate the commercial salt is treated as follows:—

The nitrate of uranium often contains phosphate of uranium and ferric nitrate. It is necessary to get rid of the foreign products.

The commercial salt is to be dissolved and precipitated with carbonate of soda, which re-dissolves the oxide of uranium and precipitates the phosphate and oxide of iron.

Saturate the filtered liquor with nitric acid, and re-precipitate the oxide of uranium with ammonia. Wash it with distilled water by decantation, re-dissolve it in nitric acid, as exactly as possible, evaporate, and crystallise.

The crystals are taken up by ether, which often leaves a little insoluble residue. Filter and evaporate the ether. The remaining salt is perfectly pure.

The uranium solution prepared as above is much more sensitive than that prepared with the acetate of uranium, as recommended by Neubauer, and this acetate solution should never be used.

The phosphate solution for determining the strength of the uranium solution is prepared from pure acid phosphate of ammonium, a salt which is easily procured. This acid phosphate contains 61.74 per cent P_2O_5 ; 8.1 grms. pure dry acid ammonium phosphate dissolved to 1000 c.c. corresponds to 0.005 P_2O_5 in 1 c.c.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

UNIVERSITY COLLEGE, LONDON.

CHEMICAL AND PHYSICAL SOCIETY.

Ordinary Meeting, Thursday, October 21st, 1886.

“An Improved Form of Weight Burette.” By Mr. G. N. HUNTLY.

The apparatus consists of an ordinary burette into the neck of which is ground a glass stopper joined on to a capillary tube, in which is blown a small bulb about half an inch from the stopper. The burette is filled up to a mark on the capillary tube just below the bulb. It is then used in the ordinary way, and then filled up to the mark from a weighed quantity of the solution. By this means results correct to 0.001 c.c. can be obtained.

The apparatus is especially useful where it is necessary to add a known excess of a solution and then titrate backwards. N/1 solution can be added and titrated back with N/100 with great accuracy.

In standardising the solution the result must be expressed as parts in 1 grm., not, as is usual, in 1 c.c.

When it is desired to use this as an ordinary burette the attachment acts as a stopper, and in the case of solutions of stannous chloride, cuprous chloride, &c., where contact with the air is prejudicial, an absorption tube can be fitted to the end of the capillary tube.

CORRESPONDENCE.

WATTS'S DICTIONARY.

To the Editor of the Chemical News.

SIR,—There is, in the paragraph on "Castor Oil," in the Second Supplement to Watt's "Dictionary of Chemistry," p. 270, a mistake so singular that it seems worth correcting, especially as it has been transferred, with the paragraph, to a recent work on Oils.

In the place mentioned a statement is made about "Italian and Ostend castor oil:" now, without referring to the original statement of Popp in the *Archiv der Pharmacie*, one may be sure that "Ostindioch" (or the contraction Ostind.) was the word used; and that East Indian, and not Ostend, castor oil is intended.—I am, &c.,

W. H. DEERING.

Chemical Department, Royal Arsenal,
Woolwich, October 23, 1886.

FLAME SPECTRA.

To the Editor of the Chemical News.

SIR,—Noticing a letter from Mr. G. G. M. Fielding in the last issue of the CHEMICAL NEWS (vol. liv., p. 212), referring to the difficulty of obtaining a continuous spectrum by means of the Bunsen flame, I have long since discarded the Bunsen burner for this purpose, and have used for some years past a jet of pure hydrogen from a No. 3 blow-pipe jet, giving a flame about $1\frac{1}{2}$ inches long and $\frac{3}{8}$ inch in diameter in its broadest part. The substance to be examined is introduced on a platinum wire in the usual manner, with or without treatment with HCl, &c., as occasion requires. The hydrogen is generated from an ordinary lead apparatus on the displacement principle, and is at all times ready for work. A good supply of zinc (free from arsenic and antimony) is placed on a suitable tray in the gasometer, and the H_2SO_4 renewed about once a week.

I have found the above method gives a continuous spectrum and satisfactory results for all ordinary purposes. When a greater heat is required oxygen is introduced under pressure and the mixed gases burnt.—I am, &c.,

G. A. MILNE, F.C.S.

Malton, October 25, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 15, October 11, 1886.

Purification of Yttria.—Lecoq de Boisbaudran.—Taking as his starting point an earth differing very little from that of M. Cleve, he submitted it to 32 fractionations with ammonia. The last precipitate was then subjected to 26 fractionations with oxalic acid. The last products

thus obtained yield, after ignition, a very white earth; the spectrum of its sulphate no longer shows, in an appreciable manner, the red, green, blue and violet bands of the spectrum described by Mr. Crookes. The lemon band of Za alone is still visible, though faint.

Fluorescence of the Compounds of Bismuth exposed to the Electric Effluve in a Vacuum.—Lecoq de Boisbaudran.—Bismuth sulphate, previously heated to dull redness, does not fluoresce in a vacuum. A very small quantity of bismuth sulphate communicates to calcium sulphate the property of emitting a very fine fluorescence of an orange red. Bismuthiferous calcium carbonate yields only a violet fluorescence, differing little from that produced without the bismuth. With bismuthiferous strontium sulphate the fluorescence is still more brilliant than with the calcium salt, and inclines to an orange. Bismuthiferous barium sulphate gives a very fine fluorescence of a red less inclining to orange than that obtained with the calcium salt. Bismuthiferous magnesium sulphate fluoresces with a still more purely red light.

Reciprocal Relations of the Great Agents of Nature.—E. Schwœrer.—A notice of Prof. Klein's comments on the Inaugural Address of Prof. Clausius as *Rector Magnificus* of the University of Bonn, and on M. Hirn's recent work, "The Notion of Force." Clausius explained the difference between the ideas anciently held in physics concerning the agencies of nature, such as heat, electricity, and light, &c., and those which are now substituted for them. Without ignoring the connection between these agencies he shows the impropriety of such expressions as "transformation of heat into electricity and of electricity into light." The propagation of radiant heat and light may very probably be explained by an action of electric forces, and that very probably electricity itself may be substituted for the *ether* supposed to fill and pervade both space and all bodies. Prof. Clausius suggests that besides ponderable matter, there exists only one substance, and that the totality of phenomena may find their explanation by means of the varied movements of this substance. Prof. Klein thinks that M. Hirn has taken a further step by considering "force" taken in general as a class of elements specifically distinct from so-called ponderable matter, establishing that the ancient imponderables of physics, electricity, heat, &c., are not particular species of matter or vehicles of force, but forces properly so-called forming a class in common with the cause of gravitation.

Saturation of Normal Arsenic Acid with Lime-Water and Strontia Water.—Ch. Blarez.—Arsenic acid and lime water form six successive stages of saturation. Baryta water behaves in a different manner, which the author is engaged in examining.

Contribution to the Study of the Alkaloids.—Oechsner de Coninck.—The author has recently shown (*Comptes Rendus*, June 21 and July 5, 1886) that the iodo-methylates, iodoethylates, &c., of the pyridic alkaloids give rise, in presence of potassa, to very sensitive coloured reactions. If we prepare piperidin iodomethylate (which is known to be a pyridin hexahydride) and treat it as has been done for the pyridin iodomethylate, no coloured reaction is produced. This is a very simple method for distinguishing a pyridic alkaloid from its hexahydride, and we may, without doubt, establish a difference of the same kind between cicutine and the corresponding collidine (conyrine). The same reaction enables us to distinguish the pyridic alkaloids from their aromatic isomers. Another reaction differentiates the pyridic alkaloids and their hexahydrides on the one hand and their aromatic isomers on the other. If we add to the iodomethylate of a pyridic alkaloid some fragments of potassium hydroxide, then water enough to form a pasty mass, which is then heated, a characteristic odour is developed, due to the formation of pyridic dihydrides. If the iodomethylates of piperidine, cicutine, aniline, orthotoluidine, metaxylidine, &c., are

treated in a similar manner, this characteristic odour is not produced.

Journal de Pharmacie et de Chimie.
Vol. xiv., No. 5, September 1, 1886.

The Presence of Lecithine in Plants.—E. Haeckel and F. Schlagdenhauffen.—Already noticed.

On Cows' Milk, Normal and Pathological; Analysis, Watering, Albumenoid Matters.—Henri Lajoux.—The author complains of the tendency of chemists to take "total solids" as the standard of the purity of milk. He proposes, instead, the total albumenoid matters. He uses in his analyses that archaic instrument the lacto-densimeter: he determines total fixed matters by evaporation at 95°; saline matter by incineration; milk-sugar by means of Laurent's polarimeter, after clarification by means of lead acetate; butter by extraction with ether, after desiccation along with sand, and albumenoids by difference.

Analysis of the Liquid of a Cyst.—P. Macquaire.—The liquid contained paraglobuline, fibrinogen, albumen coagulable by heat, and albumen coagulable by nitric acid only.

On Simple Processes for Detecting Silver, Nickel, and Tin deposited in Thin Layers on Metallic Objects.—L. Lonton.—Already noticed.

Justus Liebig's Annalen der Chemie,
Vol. ccxxxv., Part 3.

Communications from the Chemical Institute of the University of Bonn.—These consist of memoirs on the behaviour of certain diazo- and diazo-amido-compounds, by O. Wallach; and on a method for easily obtaining organic fluorine-compounds, by the same author.

The Action of Bromine and Water on the α -Meta-isocymol-sulph Acid, and on the Constitution of the α and β Meta-isocymol-sulph Acids.—Kelbe Werner and Czarnomski.—This investigation shows that in meta-isocymol only two atoms of hydrogen, and always the same, can be replaced by the sulpho-group, or by bromine if the sulpho-group has been already introduced. On dissolving meta-isocymol in sulphuric acid the sulpho-group enters in place of the hydrogen atom 4 or 6. If bromine acts upon the α -cymol-sulph acid (SO_3H being in 6) it is substituted for the hydrogen atom 4; if it acts upon β -cymol-sulph acid (SO_3H in 4) it is substituted for the H atom 6. If α -bromcymol (Br in 6) is dissolved in sulphuric acid, the sulpho-group is substituted for the H atom 4. If, on the other hand, β -bromcymol (Br in 4) is dissolved in sulphuric acid, the H atom 6 is replaced by the sulpho-group.

Action of Aluminium Chloride.—R. Anschütz.—A continuation of the extensive memoir commenced in the previous number.

The Combinations of Nitrogen with Gold.—F. Raschig.—All the three oxides of gold, Au_2O , AuO , and Au_2O_3 , yield explosive compounds with ammonia. That of the monoxide has been obtained by the author for the first time. For this compound he proposes the name sesquihydraurylamine, and for the body extracted from it by boiling water the name trihydraurylamine.

The Iodalkylates of Sparteine.—E. Bamberger.—The author has obtained a mono-iodhydrate of sparteine, the compound previously described by Mills being sparteine-iodethylate hydriodate.

Biedermann's Central Blatt fur Agrikultur Chemie.
Vol. xv., Part 6.

Formation of Saltpetre Earths in the Tropics.—A. Muntz and V. Marceno.—From the *Comptes Rendus*.

Difference of Temperature between Town and Country.—J. Hann.—The author has obtained comparative observations for Vienna, Budapest, Cilli, Linz, Munich, Perpignan, St. Louis (Missouri), and Calcutta. From these data it appears that the yearly mean temperature in a town is, with rare exceptions, higher than in the adjoining country. This excess varies from $\frac{1}{2}^\circ$ to 1° , and seems to depend less on the size of the town than on the surroundings of the station for observation. Both the daily and the absolute fluctuations are smaller in towns than in the open country.

The Oxidation of Ammonia in Waters and Soils.—J. Uffelmann.—The author proves that the oxidation of ammonia can take place without the co-operation of microbia, at least in cases of strong surface attraction. Experiments with spring-water and with the water of the Rostock town supply, showed that even in water not free from germs, and in vessels not sterilised, the oxidation of ammonia takes place much more slowly than it is commonly assumed.

Influence of Gypsum upon the Formation of Saltpetre.—R. Warington.—Evidently from an English source.

Experiments on the Cultivation of Barley.—Dr. Rehm.—Not suitable for abstraction.

The Nutritive Value of Certain Products of the Digestion of Albumen, and on the Value of the So-called Meat Peptones.—S. Pollitzer and Prof. M. Zuntz.—Peptones and the hemi-albuminose have about the same nutritive value as meat, and the assimilation of nitrogen which ensues on their ingestion forms a striking contrast to the loss of nitrogen which ensues on a diet containing an equivalent proportion of gelatin. The peptones of commerce, not prepared by the action of gastric juice but by the action of superheated water, have the same nutritive value as meat.

MISCELLANEOUS.

Franklin Institute.—We have received from the Secretary of the Franklin Institute of the State of Pennsylvania the Announcement and Programme of Lectures at that Institute for 1886-87. The Course of Lectures comprises the subjects of Chemistry, Electricity, Mechanics, Metaphysics, and the Arts and Manufactures, and we note as a sign of the times that two Lectures on Chemistry applied to Plant-Life are to be delivered by Miss Helen Abbott. The Programme is very neatly got up, and managers of similar institutions in England would do well to follow such a good example.

Non-Acid Components of Bees'-Wax.—Fr. Schwalb.—Bees'-wax, in addition to the higher fatty acids and alcohols, contains two hydrocarbons, two of which, having the melting-points 60.5° and 68° , have been isolated by the author, and are probably identical with Krafft's normal heptacosan and hentriacontan. The alcohol of wax having the highest melting-point, to which Brodie ascribes the formula $\text{C}_{30}\text{H}_{62}\text{O}$, is more probably $\text{C}_{31}\text{H}_{64}\text{O}$, whilst Brodie's formula seems to suit the alcohol of carnauba wax. In addition to myricylalcohol there exists in bees'-wax ceryl alcohol and a third alcohol, $\text{C}_{24}\text{H}_{50}\text{O}$.—*Liebig's Annalen*.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 1st.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "What shall we do with our Tar?" by Mr. L. T. Wright, C.E.

THURSDAY, 4th.—Chemical, 8. "Researches on the Laws of Substitution in the Naphthalene Series—No. II.," by Dr. H. E. Armstrong, W. P. Wynne, B.Sc., and S. Williamson. "The Hydrolysis of Sulphonic Acids" and "The Action of Bromine on Toluene-Parasulphonic Acid," by Dr. A. K. Miller.

THE CHEMICAL NEWS.

VOL. LIV. No. 1406.

THE PRESERVATION OF GASES OVER MERCURY.*

By HAROLD B. DIXON, M.A., F.R.S.

CAN gases be preserved for any considerable time over dry mercury? Faraday has told us that it is impossible; Sir Humphry Davy has maintained the contrary.

When I began experimenting with gases, ten years ago, I was under the influence of Faraday's teaching, confirmed, as it seemed to be, by the readiness with which a gas, enclosed in a vessel over mercury, will find its way along a platinum wire bent so as to connect it, through the mercury, with the outer air. At first I hesitated before using any gas which had been collected a few weeks previously; but, as analysis showed no alteration in the gases, I concluded that the ordinary process of inter-diffusion must be slower than that found by Faraday. As weeks lengthened into months, and still no alteration could be detected in the tubes, I became sceptical of any diffusion taking place, and after a couple of years I became convinced that if any diffusion took place at all, it was too slow to sensibly affect the results of an analysis made with a sample of gas collected within twelve months.

In Dr. Bence Jones's "Life of Faraday" a passage occurs which shows that Sir Humphry Davy did not accept Faraday's results. In 1823 Faraday had filled five dry bottles over mercury with a mixture of oxygen and hydrogen. These bottles had been examined in the following year, and a considerable alteration had been detected in the confined gas. From this experiment Faraday concluded "that mercury cannot confine gases perfectly." Davy, dissatisfied with the conclusion, repeated the experiment. The last entry in the Laboratory note-book of the Royal Institution, written by Sir Humphry Davy's hand, is dated February 5, 1826:—

"Experiment of July, 1825, examined. The hydrogen, confined by mercury, whether in a bottle with a stopper, or merely confined by dry mercury, contained no common air."

Faraday also repeated his experiment. On June 28th, 1825, he partially filled three vessels with a dry mixture of oxygen and hydrogen over the mercurial trough. The vessels were 3-ounce glass bottles with well-fitting ground stoppers, well cleaned and dried. No grease was on the stoppers. The bottles were filled four-fifths full of the mixed gases, the rest of the space being occupied by the mercury. The stoppers were then replaced "as tightly as could be," the bottles put into glasses in an inverted position, and mercury poured round the stoppers and necks, rising not quite up to the level of the mercury within. The bottles were then "sealed up" in a dark cupboard.

On September 25th, 1826, after fifteen months, the bottles were opened and examined. The mercury still remained higher inside than outside.

I. Part of the contents transferred in the mercury trough proved to be common air. No trace of the original mixture remained.

II. The mixture was still explosive. Spongy platinum was brought to dull ignition in it: no explosion took place, but the volume diminished to rather less than one-half. The residue supported combustion little better than common air. Hence nearly half the mixture had escaped.

III. The mixture was explosive. It contained nearly two-fifths of a mixture of oxygen and hydrogen, the rest being very little better than common air.

Faraday concludes there is "no reason to suppose that this capability of escape between glass and mercury is confined to the mixture of hydrogen and oxygen. Probably every gas having no action on mercury or glass would have made its way out in the same manner."*

Apart from the interest naturally attaching to a point in dispute between two such masters of their craft as Davy and Faraday, the settlement of this question is of some importance to all chemists who work with gases. After reading the passages referred to in the "Life of Faraday," it occurred to me that I might have the data for deciding between the two conclusions, for I had kept the unused residues of several samples of different gases which had been prepared at various times since 1876. An analysis of these gases would show whether any appreciable diffusion had gone on between the contents of the tubes and the outer air, and the long period for which some of the samples had been kept afforded the condition of time necessary to give accuracy to the results. If it should be found that gases had remained over mercury not appreciably altered for periods up to ten years, it seemed to me that the question might be answered unhesitatingly in Davy's favour; but if Faraday's view were correct, the analyses would not only show this, but would afford some idea of the average rate of the slow gaseous diffusion between the mercury and the glass.

I resolved therefore to analyse all the samples of gas I had remaining which had been kept for periods longer than two years. On examining my cupboards I found the following samples;—

Two tubes, electrolytic gas, prepared Jan., 1877.

Two tubes, cyanogen, prepared Aug., 1878.

One tube, sulphurous acid, prepared Feb., 1880.

I was disappointed at finding no other samples prepared by myself of over two years' standing; the hydrogen, carbonic oxide, and oxygen tubes had been used and replenished within the last two years. But a search through other cupboards in the laboratory revealed a stand of five tubes filled with hydrogen, bearing the date May, 1884. These tubes had evidently been filled by one of my pupils in a class for gas analysis which I held during that month. There was no name attached, and I cannot recall the handwriting on the label. The contents of these hydrogen tubes were first determined by exploding them with excess of oxygen. The numbers attached to the analyses give the order in which the tubes had been originally filled with the gas, which was prepared by the electrolysis of dilute hydrogen sulphate:—

	1.	2.	3.	4.	5.
Percentage of hydrogen ..	93.6	96.0	97.3	99.4	99.7

These analyses are not conclusive as to the preservation of the gas intact over mercury, but, looking to the regular increase in the percentage of hydrogen found, I think the most probable interpretation of the numbers is that the collection of the gas was begun before all the air had been swept out of the apparatus, and that the gases were found in the tubes in the same condition as when they were collected two years and three months previously.

The sulphurous acid collected in 1880 was next examined. The gas was almost completely absorbed by solution of potash, the contraction being 99.4 per cent.

The two samples of cyanogen collected in 1878 were exploded with excess of oxygen, and the carbonic acid formed was absorbed by solution of potash. The first sample showed a slight contraction on explosion, and the volume of gas absorbed by the potash, calculated as carbonic acid, gave 100.68 per cent of cyanogen. The second sample showed no alteration of volume on explosion, and the volume of gas absorbed by potash, calcu-

* A Paper read before the British Association, Birmingham Meeting, Section B.

* *Quart. Journ. Science*, xxii., 229.

lated as carbonic acid, gave 99.79 per cent of cyanogen. These numbers agree with the results of several analyses I have made with freshly prepared cyanogen, a small quantity of nitrogen—varying in amount with the excess of oxygen used—being oxidised in the explosion.

The two samples of electrolytic gas, prepared in January, 1877, were found on explosion to contain 98.95 and 98.86 per cent of explosive gas. A sample of electrolytic gas, prepared a month ago with the same apparatus, was found to contain 98.91 per cent of explosive gas.

The analyses of these five samples of gas, collected 6½, 8, and 9½ years ago, are sufficient to show that gases may be preserved over mercury without suffering in any appreciable degree from diffusion. If diffusion had taken place at all in these cases, it was too small to be detected by careful analysis after several years; so that we seem forced to conclude that diffusion, in the sense used by Faraday, does not take place between mercury and glass under the conditions of these experiments.

Everyone will agree that Faraday's manipulative skill precludes all idea of any accidental contamination of the gases he used; everyone will agree that the results he found are the true expression of the facts of the case before him. The question therefore arises—How do the conditions of his experiments differ from those of mine? In my experiments the gases were collected in *hot* tubes filled with *hot* mercury. The mercury in the trough was kept from 70° to 90° C. Each tube was brought hot from the oven as it was required; a card, cut to fit the trough, was drawn through the mercury, leaving behind it a brilliant clear surface of the liquid. Into the surface so cleared the open end of the tube was plunged. The tube was then depressed into the mercury, and filled by inversion below the surface, a leathern glove protecting the operator's hand. The tube, still containing a few small bubbles of air, was then filled with the gas, and was again charged with mercury by depressing it under the liquid. After being filled a second time with the gas, the end of the tube was passed into a small crucible which had been heated before being introduced into the mercury. The tube and crucible were then removed from the trough to a wooden stand.

Faraday makes no mention of his having heated his mercury and glass vessels, so that it is probable that the glass may have had a slight coating of moisture upon it, and it is possible that the mercury may have had a fine film of impurity on its surface. Such a film sticking to the glass, whether of moisture or of impurity on the metal, may have made the means of communication between the enclosed gases and the air outside.

Post Scriptum.—Since reading this paper I have repeated an interesting experiment described to me by Prof. McLeod. It throws light on the action of a film formed between glass and mercury. Air is drawn through a U-tube filled at the bend with pure mercury. The air passes through the liquid in large bubbles, throwing the mercury up the tube and breaking it into globules. A thin strip of clean sheet lead is now dropped into the mercury. In a minute or two the bubbles of air diminish in size, and the column of mercury is less disturbed. After about ten minutes the air passes in a continuous stream between the glass and mercury, and with so little commotion that the passage of the air would be almost invisible but for the quivering vibration on the surface of the liquid. An unbroken passage is formed between the glass and the impure surface of the mercury.

By reference to Faraday's "Chemical Manipulation" (New Edition, 1830) I find that Faraday was aware in 1830 of the action of the films on impure mercury. In par. 1279 he writes:—

"The manner in which these films interfere with experiments made over the mercurial trough is principally by preventing contact between the metal and the jars used. If a jar be dipped into the mercury, it does not break through the film and come into contact with the pure

metal beneath, but the film expands between the glass and the metal, and, from its comparatively solid and rigid nature, entirely prevents that close contact which would occur between pure mercury and the glass."

In the discussion which followed the paper Mr. CROOKES and Sir HENRY ROSCOE gave it as their opinion that the purity of the mercury was the essential condition for preventing diffusion, which depended on the formation of a film between the mercury and the glass.

Mr. TURNER said that the experience of Dr. Frankland confirmed the opinion of Mr. Crookes and Sir H. Roscoe, that diffusion did or did not take place according to the state of the mercury and of the containing vessel.

Mr. A. G. VERNON HARCOURT said that it might have been supposed that dirty mercury, from its known property of adhering to glass, would have been most efficient in preventing diffusion. This, however, did not appear to be the case, and he suggested that some comparative experiments should be made with pure and with dirty mercury.

Dr. GLADSTONE said that when talking on this subject some years ago to a friend, he was answered that, if gas could not be retained without diffusion, then we could have no mercurial barometer.

Prof. H. MCLEOD pointed out that dirty mercury, though it appeared to adhere closely to glass, did not really do so, but allowed a passage between the film and the glass surface. The standard barometer at Kew had been prepared with hot mercury, and though constructed many years ago it was believed to be perfectly accurate.

Dr. S. YOUNG said that his experience with barometers, which was considerable, showed that some barometers remained perfectly correct, while others did not.

ON THE DISTRIBUTION OF THE NITRIFYING ORGANISM IN THE SOIL.

By R. WARINGTON.

PREVIOUS experiments, conducted at Rothamsted on this subject (*Trans. Chem. Soc.*, 1884, p. 645), had led to the conclusion that the nitrifying organism is always to be met with down to 9 inches from the surface, and that at 18 inches it is sometimes present; but experiments with soil 2 to 8 feet from the surface failed to yield evidence of the presence of the organism.

Further experiments have been made in 1885, and during the present year, both in the field with the stiff clay subsoil previously worked on and in another field having a loamy subsoil; in all sixty-nine new experiments have been made. The soil in the previous experiments was removed, with suitable precautions, from a freshly cut surface, and placed in sterilised solutions consisting of diluted urine (0.4 per cent). It having since been found that the facility with which urine nitrifies is greatly increased by the presence of gypsum (*Trans. Chem. Soc.*, 1885, p. 758), an addition of a small quantity of gypsum was made to the solutions employed in all the recent experiments; rather larger quantities of soil were also employed. The results may be summarised as follows:—

Depth of soil.	Number of expts.	Number of solutions nitrifying.	Number nitrifying out of 10 trials.
Less than 2 feet	17	17	10.0
2 feet	11	11	10.0
3 "	11	10	9.1
4 "	11	7	6.4
5 "	2	1	5.0
6 "	9	4	4.4
7 "	2	0	0.0
8 "	6	0	0.0

* Read before the British Association, Birmingham Meeting, Section B,

Six of the above experiments were made with chalk, which underlies the Rothamsted subsoil; the chalk was from depths of 5, 6, 7, and 8 feet. None of the samples of chalk produced nitrification.

The new results show a far deeper distribution of the nitrifying organism than was concluded from the earlier experiments. The power of producing nitrification is now found to exist generally down to 3 feet from the surface. Below this point the occurrence of the organism becomes less frequent, though at 5 and 6 feet about half the trials resulted in nitrification. With soil from 7 and 8 feet no nitrification was obtained. The considerable difference between the earlier and later results is to be attributed to the employment of gypsum in the later solutions. The nitrifying organism in the subsoil is indeed less abundant, and probably much more feeble than in the surface soil, and is apparently unable to start nitrification in the decidedly alkaline solution which urine produces in the absence of gypsum.

Although it appears that the nitrifying organism may exist at considerable depths, nitrification is practically confined to the surface soil. The quantity of nitrogen as nitric acid annually obtained in the drainage water from soils of different depths in the drain gauges at Rothamsted is on an average of nine years:—

Soil 20 inches deep	40.2 lbs. per acre
Soil 40 " "	35.0 " "
Soil 60 " "	38.8 " "

There is no evidence here of a greater production of nitrates when the subsoil is included in the experiment.

Nitrates are always found most abundantly in the surface soil unless heavy rain has occurred to wash them downwards. Two fallow soils at Rothamsted were found to contain the following quantities of nitrogen as nitrates in lbs. per acre:—

1st 9 inches	28.5	40.1
2nd " "	5.2	14.3
3rd " "	—	5.5
Total	33.7	59.9

THE COLOUR OF THE OXIDES OF CERIUM AND ITS ATOMIC WEIGHT.*

By HENRY ROBINSON, M.A.,

Assistant to the Professor of Chemistry, in the University of Cambridge.

At the Meeting of the British Association at Montreal I had the honour to submit to this Section a paper on the atomic weight of cerium. On that occasion I did not say anything about the colour of the oxides of cerium: Wolf had stated he had prepared a white oxide, and I thought it possible there might be an oxide of that colour. My subsequent experiments have not confirmed that opinion.

Before Wolf commenced his investigation it had been recognised that the brown colour of the mixed oxides obtained from cerite, or from other sources of cerium, was due to the presence of didymium, and it had been found that the more completely the didymium was removed from them the lighter became the colour of what was left. "Still at the best," quoting from Clarke's "Constants of Nature," "a faint colour remained which was supposed to be characteristic of the oxide itself. In 1868, however, some experiments of Dr. Wolf were posthumously made public, which went to show that pure ceroso-ceric"—or, as it is called now, ceric—"oxide is white, and that all samples previously studied were contaminated with some other earth, not necessarily didymium, but possibly a new substance, the removal of which tended to lower the ap-

parent atomic weight of cerium very perceptibly." Further on he says "The last oxide was perfectly white," and again, at the end of the article on cerium, "It is now clear that new determinations are needed, made with a material yielding *white* ceric oxide." It seems to me that discrimination has not been made between that lighter colour which follows the gradual removal of didymium and that "faint colour supposed to be characteristic of the oxide itself."

When didymium is gradually removed the oxides decrease in colour from a dark brown to a faint reddish brown, which tinges the yellow ceric oxide when the least trace of didymium is present: the faint colour is a very pale sulphur-yellow, altogether free from brown or red.

It is probably owing to the great prominence given by Clarke to Wolf's work that the somewhat prevalent notion obtains that cerium has a white oxide; possibly the opinion that such is the case has been strengthened, or even begotten in some cases, by the fact that cerous salts with colourless acids are white. But it is by no means true that a coloured base with a colourless acid need give a coloured salt. To take two instances—cuprous oxide is red, cuprous chloride is pure white; silver oxide may be bluish, or brown, or black, according to the way in which it has been prepared, but its chloride, nitrate, and sulphate are white. I think that any inference that even cerous oxide is white because its salts are white may be dismissed without further consideration. Besides, when hydrogen is passed over heated ceric oxide, the oxide becomes darker in colour, dark grey or almost black, water being formed at the same time.

I will now return to Wolf's work, and I think I shall be able to show that some great mistakes have been made. In the first place, his mode of separation was an improper one, and would not result in the production of a pure cerium salt; secondly, his method of analysis would not give correct results, as Brauner has already proved by experiment; and thirdly, if the atomic weight of his metal was 137, or anything near that number, it was not an oxide of cerium at all. Wolf's mode of separation was as follows:—He first prepared, from Swedish cerite, basic cerium sulphate, by Bunsen's well-known method, mixed with a considerable quantity of didymium and lanthanum sulphates. He dissolved and re-precipitated it several times as basic sulphate, rejecting the mother-liquor. The method so far was good. Bunsen says if it is persevered in, in the end a very small quantity of pure basic sulphate of cerium may be obtained. He next dissolved the precipitate, which he says still contained a considerable quantity of didymium, and which, my own experience tells me, would also contain a good deal of lanthanum by adding a little sulphuric acid. He then reduced the ceric sulphate by sulphurous acid, and drove off the water and excess of acid by heat. His method from this point, although he made one or two slight deviations, was essentially as follows:—The mixed sulphates were dissolved in water, and fractionally crystallised many times by gently evaporating their solution on a water-bath; the mother-liquor was rejected each time. And here was the first mistake; he fell into an error similar to that a certain manure manufacturer is said to have done. It is related of the latter that, attending a lecture on agricultural chemistry, he heard there that ammonium sulphate might be economically prepared by mixing gypsum with the ammoniacal liquid from gas-works. He went to his works, and proceeded to utilise his newly-acquired knowledge; he mixed gypsum with the gas-liquor as directed, left it to stand for a time, and then, like Wolf, he too threw away his mother-liquor, and, after carefully drying the precipitated calcium carbonate and other worthless substances, sent it out to his unfortunate customers as a very superior sample of sulphate of ammonia. He succeeded in preparing the wrong thing entirely, and so did Wolf if his oxide was white and its metal had an atomic weight anywhere near 137. My contention is that fractional crystallisation of a mixture of cerium, lanthanum, and didymium

* A Paper read before the British Association, Birmingham Meeting, Section B.

sulphates will not give cerium sulphate as an end product, but lanthanum sulphate, or a mixture of the two. The didymium will be eliminated first, next the cerium, and the lanthanum will remain behind; and this explains why Wolf obtained a white oxide, and why his atomic weight was so low. I have made some experiments to prove this, following Wolf's plan. When he arrived at the cerous sulphate stage he says a good deal of didymium was still present. I am certain no small quantity of lanthanum was there also, although he says nothing about it; indeed his whole paper goes to show he never even suspected its presence. He dissolved the whole in water, and crystallised by evaporating the solution until but little of the mother-liquid remained. The mother-liquid gave a brown oxide, the crystals a brick-red one. The process was repeated five times. The resulting mass of crystals was then fractionated by slow evaporation on the water-bath into three portions, A^1 , A^2 , and A^3 ; then A^1 into B^1 and B^2 ; and, lastly, B^1 into C^1 and C^2 . Of these fractions B^2 , C^1 , and C^2 were analysed. B^2 gave the atomic weight of cerium 138.312, C^1 138.528, and C^2 138.843. It will be seen from this the least soluble fraction of B^1 gave the lowest atomic weight.

I commenced my experiments so as to produce as nearly as possible Wolf's A^1 series of crystals. I took cerium oxalate nearly free from didymium and lanthanum, and lanthanum oxalate free from cerium but still containing a little didymium, and mixed them so that I should have four parts of Ce_2O_3 to one part of La_2O_3 . The oxalates gave me 44 grms. of anhydrous sulphates, which were dissolved in 860 c.c. of water. The solution was almost colourless, but showed plainly the didymium absorption-bands.

Wolf says he evaporated slowly on the water-bath, but he does not say at what temperature. I took care in my experiments always to conduct the evaporations as nearly as possible at 65° . The first solution was evaporated until a fair quantity of crystals had formed; then the mother-liquor, 400 c.c., was quickly drawn off by a reverse filtering-cone; another crop of crystals, A^2 , was taken from it, and then the remaining liquid, which would contain the A^3 crystals, was found to be plainly coloured by didymium, showing, as might be expected, that the bulk of it had accumulated here. The first crop of crystals, A^1 , was dehydrated, and found to then weigh 18 grms. It was dissolved in 430 c.c. of water; the didymium absorption-bands showed, but weak. B^1 was crystallised out as before, and weighed 8 grms. It was dissolved in 200 c.c. of water; the didymium absorption-bands were now very weak. C^1 was crystallised from it, and weighed 3.5 grms. as anhydrous sulphate; the mother-liquor measured 122 c.c.

The C^1 fraction of crystals should now, according to my view, contain a good deal of lanthanum. In order to determine the quantity it was converted into oxalate, and then into oxide: the latter weighed 1.6368 grms.; it was yellow. The oxide was dissolved in nitric acid; the solution was evaporated on a sand-bath until fumes of nitric oxide had been given off for some time; the dry mass was then treated with hot water and a very little nitric acid, and the soluble portion was filtered from the insoluble. The filtrate was evaporated to dryness, and was treated exactly as the first dry mass had been: what was insoluble was added to the first portion of insoluble. The whole of the insoluble, after igniting, was boiled with nitric acid, again heated until nitric fumes came off, and the soluble was again extracted and added to that already obtained; and the process was repeated until, on the one hand, an insoluble portion was obtained from which nothing more could be dissolved, and, on the other, a soluble one from which nothing insoluble could be separated. The soluble part was now converted into oxide; it was white, slightly tinged with red by the very small quantity of didymium left in it, and weighed 0.527 gm. There was so little didymium in it that it might safely for the present purpose be considered all La_2O_3 . To make sure it was dissolved

in nitric acid the solution was perfectly colourless, and on testing with hydrogen peroxide and ammonium acetate only a mere trace of cerium was found to be present. Subtracting this 0.527 gm. from the oxide first obtained, 1.10975 grms. of ceric oxide is left, and reducing this to Ce_2O_3 1.05815, so that now the proportion of cerous oxide to lanthanum oxide is as 1.05815 to 0.527, or as 2 to 1, instead of as 4 to 1 at the commencement of the experiment.

I now thought it would be well to determine the relative solubilities of cerous and lanthanum sulphates in water at the temperature I had crystallised the mixture. I took 10.643 grms. of anhydrous cerous sulphate, dissolved it in 170 c.c. of water at the ordinary temperature,—it was about 20° ,—evaporated the solution on the water-bath at from 60° to 65° . In this and the following experiment I took care that the ring on which the evaporating dish was placed was much smaller in diameter than the surface of the liquid in the dish, and also that the diameter of the evaporating dish was less than that of the water-bath: by this means I prevented a ring of sulphate forming where the surface of the liquid touched the side of the dish. Had this precaution been taken in the previous experiments I am persuaded the proportion of Ce_2O_3 to La_2O_3 would have been less even than it was. The solution was much reduced in volume before crystals began to appear. When a good quantity had formed I filtered the liquid through a dry filter placed in a funnel surrounded by a hot-water jacket into a 50 c.c. flask placed in water at 65° , the liquid remaining after the 50 c.c. was filled to the mark measured 17 c.c. The amount soluble in 100 c.c. of water at 65° was 10.2958 grms. of anhydrous sulphate.

I then made an exactly similar experiment with lanthanum sulphate. 6.306 grms. of the anhydrous sulphate were taken, and dissolved in 190 c.c. of water at about 20° . After standing about twenty-four hours some crystals had already formed. On evaporating the solution, tufts of crystals began to appear before its temperature reached 60° . After about the same quantity of crystals seemed to have formed as when the evaporation of the cerous sulphate was stopped, the liquid was filtered, everything being done as in the previous experiment, into the 50 c.c. flask, but the liquid remaining in this case, after filling the 50 c.c. flask, measured 80 c.c. 100 c.c. of water at 65° held in solution 2.106 grms. of La_2SO_4 . So that the solubility of cerous sulphate at this temperature is nearly five times as great as that of lanthanum sulphate.

I think these experiments show pretty conclusively that Wolf's method was not one by which pure cerous sulphate could be obtained. Wolf's determination of the atomic weight of cerium is based entirely upon the amount of ceric oxide he obtained from what he supposed was the anhydrous sulphate. He dehydrated his crystals by heating them in a small platinum crucible placed in a larger one over a naked flame. Bührig has shown that this would not effect the desired end; that at a moderate temperature the water is not completely driven off; and that at a slightly higher one the salt is decomposed.

Brauner also found this to be the case. He says at 500° the salt may lose a trace of sulphuric acid, or it absorbs some oxygen and becomes heavier and slightly yellow. He overcame the difficulty by heating the salt in a sulphur-bath; at 440° , the temperature of boiling sulphur vapour, the dehydration was complete, and no decomposition of the sulphate could be detected. His method and apparatus are described in the *Transactions of the Chemical Society*, 1885. Thus the real composition of Wolf's anhydrous sulphate becomes very doubtful. He dissolved the anhydrous sulphate in water and precipitated the cerium as oxalate, and determined the amount present as CeO_2 .

Wolf's number for the atomic weight of cerium depends entirely on the amount of ceric oxide thus obtained, for the sulphuric acid was not estimated; at any rate there is not a single scrap of evidence to show it was. One thing goes against my theory that this white oxide was La_2O_3 ,

or a mixture of it and CeO_2 , with a preponderance of the former. In Wolf's paper this passage occurs:—"The resulting ceroso-ceric oxide was always analysed, and the amount of cerous oxide corresponding with it determined according to Bunsen's volumetric method by iodide of potassium and chlorhydric acid from the amount of liberated iodine"; and this statement, for instance, is made "(1) 1.4542 grms. of B^2 gave 0.19419 grms. water and 0.76305 grms. ceroso-ceric oxide, corresponding with 0.72443 grms. cerous oxide," but no details are given; nothing is said about what precautions were taken to ensure accuracy in measurements, or even how the information obtained was made use of. The analysis might be only qualitative, and the statement would still remain true. I have gone through the numbers, and have found that there are curiously constant errors for each different series, which lead me to suppose that the amounts of cerous oxide corresponding to the ceric oxide found were calculated; it matters little what equivalents are taken in doing so, for the differences for different equivalents are almost inappreciable. This phantom white oxide seems to have led men's minds astray. Wolf evidently felt bound to find a white oxide and a low atomic weight. What he considered his purest salt gave 136.992 as the atomic weight of cerium, but re-calculated by Clarke it became 138. Brauner says his purest oxide was white, but he preferred to call it the "palest chamois." The latter description would apply to my oxide, but I prefer to call it a pale sulphur yellow: his and my atomic weights were practically identical, being 140.2210 and 140.2593 respectively.

Mr. Crookes* has lately obtained a white ceric oxide, but, unlike Wolf's, his atomic weight is high, 141.1; whilst Bührig, whose atomic weight was also high, 141.228, had a yellow oxide.

The apparent colour depends much on the physical state of the oxide; an oxide decidedly yellow in a lumpy state becomes pale when finely powdered; but the preponderant opinion among observers is that, even in the finest powder, ceric oxide is not really white.

ON THE PRODUCTION AND MEASUREMENT OF GOLD AND OTHER MINUTE METALLIC SPHERES TO DETERMINE THEIR WEIGHT.

By G. A. GOZDORF.

IN making assays for gold where the amount of gold is very small a little silver is required in which the gold may be collected. As nearly all commercial litharge contains silver it is rarely necessary to add any separately for this purpose. The litharge I at present use contains at the rate of 6 dwts. of silver and $\frac{1}{4}$ of a grain of gold per ton.

Having obtained a prill in which the amount of gold is a third or less than the silver, the prill is boiled in dilute nitric acid in a porcelain capsule to dissolve the silver, and where the amount of gold is more than 1 dwt. to the ton a second boiling in strong nitric acid should be given. If care is taken in using dilute acid at first and boiling gently the gold will be left in one piece of a nearly black colour. The acid is now decanted off and the gold washed two or three times in distilled water. The gold may be now placed on an aluminium or other polished metal plate by inverting the capsule and leading the last drop of water and the gold with a glass rod on to the plate, the water is drawn off by a piece of filter-paper, and the plate gently heated till dry.

Having thus obtained the gold in a pure state a bead is made of boracic acid on a platinum wire loop and pressed on the gold while still red-hot; the gold adheres without

difficulty, and by heating the bead before the blowpipe the gold is obtained as an almost perfect sphere.

Should the resulting sphere of gold be very minute it is better to measure it under the microscope while in the bead, but if large enough to be seen with the naked eye it can be measured more accurately after dissolving the boracic acid bead in a watch-glass with hot water and placing the sphere of gold on a glass slide.

The plan of measuring minute prills of silver and gold to determine their weight was first introduced by Harkort, who used an ivory scale engraved with two fine lines meeting at an acute angle and divided into fifty equal parts.

According to the fifth edition of Plattner's "Probirkunst," p. 520, Goldschmidt determines the weight of silver and gold prills by measurement with the microscope. As I have not access to the paper on the subject his manner of preparing the prills for measurement is unknown to me.

Harkort and Plattner, in making scales for the determination of the weight of gold and silver prills, weighed prills corresponding to the larger divisions of the scale, and from their weight calculated the weight for the smaller divisions. These prills were taken direct from the cupel, and at the point of contact are flattened, but as the amount of flattening is not always the same, and hardly varies in extent with the size of the prill, and as the converging lines on the scale cannot be very sharply defined, this method is not capable of the same accuracy as where the almost perfect spheres are measured with a microscope.

No other flux seems to possess advantages equal to those of boracic acid for obtaining a sphere of gold. Borax and other fluxes are so fluid when hot that the gold is very liable to alloy with the platinum wire; this rarely occurs with boracic acid on account of its great viscosity, even when white hot. Boracic acid is also easily soluble in water, so that the gold spheres can be separated without loss of time.

The following rules and figures may be useful to any one wishing to adopt the system here described.

1. The weight of a sphere increases as the cube of the diameter.
2. The weight of a sphere of any substance of which the specific gravity is known is obtained by multiplying the weight of a unit sphere of water by the specific gravity of the substance and the cube of the diameter.

Constants for Use with Gramme Weights.

1. Weight of a sphere of water 0.01 m.m. in diameter = 0.000,000,000,523,6 of a gm.
2. Weight of a sphere of gold 0.01 m.m. in diameter = 0.000,000,010,210,2 of a gm.
3. Weight of a sphere of gold 0.0x m.m. in diameter, $x^3 \times 0.000,000,010,210,2$ of a gm.
4. If 20 grms. of ore are taken for assay the number of grains of gold per ton is found by $x^3 \times 0.008004$, in which x = the diameter of the sphere of gold in hundredths of a millimetre.

Constants for Use with Grain Weights.

1. Weight of a sphere of water 0.001 inch in diameter, 0.000,000,132,4 of a grain.
2. Weight of a sphere of gold 0.001 inch in diameter, 0.000,002,582 of a grain.
3. Weight of a sphere of gold 0.00x inch in diameter, $x^3 \times 0.000,002,582$ of a grain.
4. 200 grains of ore being taken for assay, the number of grains of gold per ton is found by $x^3 \times 0.2045288$, in which x = the diameter of the sphere of gold in thousandths of an inch. By taking 978 grains for assay x^3 = grains of gold per ton.

To test the accuracy of the above figures a comparatively speaking large sphere of gold from an assay was measured and found to be 0.593 m.m. or $\frac{59.3}{100}$ of a m.m.,

in diameter $59.3^3 \times 0.000,000,010,210,2 = 0.002,129$ of a

* Phil. Trans., 1885, Part 2, p. 704.

gram. When weighed on a very delicate balance it was found to weigh 0.0021 gram., and as this balance does not indicate beyond the fourth decimal the results may be considered identical. This sphere indicated gold in the sample tried at the rate of 3 ozs. 9 dwts. 13 grs. per ton.

The smallest sphere of gold I have yet measured was 0.024 m.m. in diameter, and by applying the above rule the weight would be $2.4^3 \times 0.000,000,010,210,2 \times 15.43235$ (to convert grammes to grains) = 0.000,002,178, or a trifle over two millionths of a grain.

Spheres of silver may be obtained and measured in a similar manner. The boracic acid acts slightly on the silver, but the quantity dissolved is inappreciable, as the action is not prolonged. The specific gravity of silver being 10.53, the weight of 1-100th m.m. would be $0.000,000,000,523,6 \times 10.53 = 0.000,000,005,513,508$ of a gram. In a test assay made with silver the sphere measured $0.57 = \frac{57}{100}$ of a m.m., from which the weight deduced would be 0.001,020,96 of a gram., the balance showing the weight as 0.0010 of a gram.

Copper, lead, and other metals cannot be melted in boracic acid on platinum wire without dissolving to a perceptible amount, but may with care be melted in sodic carbonate, and, by dissolving the latter in hot water, the sphere of copper, &c., obtained and measured.

Adelaide, July 6, 1886.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 221.)

M. BORICKY employs hydrofluoric acid to attack those silicates which resist the action of hydro-fluosilicic acid; he, however, prefers the latter, because when applied to the polished surface of a mineral it gives better crystals, on account of its slower and less violent action, and also because it renders it possible to estimate the proportions of the component parts when the compounds formed have the same degree of solubility. It may be also well to mention that if the substance is warmed with hydrofluoric acid, in a platinum crucible, very fine crystals are obtained: as to the quantitative estimation the author himself (p. 15) only applies it in rare cases, because the solubility of the fluosilicates varies between somewhat wide limits,* and because the different minerals do not resist the action of the acid to the same degree.

This fact, that the minerals are less easily attacked in proportion to the less amount of silica they contain, can be used to separate and isolate the different mineral species in a mixture. Thus, if we treat a rock composed of felspar and augite, in which the former predominates, at first the felspar only is dissolved, but the separation is not perfect, because augite succumbs to the action of the acid after some time. A prolonged treatment with acid is necessary in order to transform the whole mass into fluosilicates. However, this method can be used advantageously when time is of no importance.

Four hours suffice for the conversion of felspar by hydro-fluosilicic acid at 3 per cent, but six or seven hours are necessary to effect the same with augite or amphiboles. As for mica, it is better to treat it with a mixture of hydro-fluosilicic acid, with a little hydrofluoric acid added to it.

If we do not wish absolutely to operate on polished surfaces, hydrofluoric acid can be used with advantage. The powdered mineral is decomposed in a few minutes by digesting it with this reagent in a platinum crucible. If, after the addition—to make more sure—of a little hydro-fluosilicic acid, we evaporate to dryness and extract

the residue with boiling water, and then place a drop of the solution on a plate of glass, we soon see the different crystals separate out.

It is clear that in this method of examination we might limit ourselves to using much smaller quantities of mineral than when following M. Boricky: in fact this *savant* made use of particles as large as a pin's head, since he was contented with a partial decomposition.

The plates of glass which are used in the experiments with hydrofluoric and hydro-fluosilicic acids, or with solutions of fluorides, should be covered with a coat of some protecting material. M. Boricky employs Canadian balsam for this purpose; for if care be taken to evaporate slowly a smooth and colourless layer is left on the glass, which resists the action of hydro-fluosilicic acid, and even weak hydrofluoric acid. It would leave nothing to be desired if the little crystals did not adhere so strongly that rinsing with water will not remove them. Washing is not advisable, as it causes cracks: thus we are obliged to use a new plate for every experiment. This constitutes, in my opinion, a real disadvantage in M. Boricky's method.

Let us now pass over the examination of felspars, the principal point of which is the detection of alkalies, and let us consider for a short time the analysis of augites and amphiboles: we shall now find the principal defects in M. Boricky's method. In this class of test we want chiefly to find and estimate calcium, magnesium, and iron; and, secondly, to try for the presence of aluminium.

Fluosilicate of lime is a very soluble salt. M. Boricky states that the crystals of this salt can be transformed, by means of sulphuric acid, into a mass of needles of sulphate of lime; and M. E. Fleischer (*Titrimethode*, pp. 34, 35) uses this salt as a reagent instead of hydro-fluosilicic acid, for the precipitation of potash and soda. We can thus easily understand that the fluosilicate of lime does not crystallise until long after the analogous salts of potassium and sodium; but I have often detected the presence of lime in two or three minutes by means of sulphuric acid, when hydro-fluosilicic acid had given no result whatever.

According to M. Boricky (p. 23) fluosilicate of sodium may possibly contain lime. This remark is quite true; but the same is also true with regard to fluosilicate of potassium, which, when separated from a mixture rich in calcium, forms crystals of gypsum on the addition of sulphuric acid, although in less quantity than the sodic salt. The cause of this phenomenon is evidently the presence of the concentrated mother-liquor, which contains fluosilicate of lime; the salt of sodium, because of its microlithic structure, being much more apt to absorb this mother-liquor than the corresponding salt of potassium.

Fluosilicate of magnesium has the same crystalline form as that of iron and manganese: we therefore expect to find, as in the case of the carbonates, mixtures of crystals forming in the solution, containing the three compounds in isomorphous combination. This, however, does not always happen to be the case. In fact I have seen fluosilicate of magnesium which was only slightly coloured by sulphide of ammonium, separate from a solution which contained as much iron as magnesium. A much greater disadvantage of this salt is its extreme solubility in water. It forms crystals with great difficulty and after a long time only, and they are very deliquescent, which property they possess in common with the ferrous salt. The want of a good method for the detection of magnesium is the principal reason which led me to try and find a new micro-chemical method.

With respect to aluminium M. Boricky (p. 15) affirms that it does not form a crystalline compound with hydro-fluosilicic acid. The fluosilicate of aluminium will not crystallise; its solution leaves a thick glutinous mass on evaporation. However, it has been found, according to M. Deville,* that the salt is not always formed. In fact,

* Potassic fluosilicate dissolves in 833 parts of water at 17.5° C.; the sodic salt requires 152 parts, and the lithic only 1.9 under the same conditions. The salts of calcium and magnesium are also extremely soluble.

* Würrz, "Dictionnaire de Chimie," article on Aluminium and Fluorides.

with excess of kaolin, hydro-fluosilicic acid forms fluoride of aluminium, and this reaction is favoured by the presence of alkaline fluorides, which, combining with the previous salt, produce chemical compounds which are quite stable and almost insoluble. If we employ a mixture of hydro-fluosilicic and hydrofluoric acids to attack the mineral, and if that contains a sufficient quantity of alkali, we can rely upon obtaining the aluminium in the form of a double salt.

Probably M. Boricky did not pay much attention to these latter bodies, because they have exactly the same crystallised form as the corresponding fluosilicate. The fluo-aluminate of potassium resembles closely the fluosilicate of potassium; fluo-aluminate of sodium forms the same hexagonal crystals (∞ P. P.) as the corresponding fluosilicate. I have satisfied myself that the prisms crowned with a pyramid are doubly refracting, while the hexagons disappear between two inverted Nicols.

I have repeated these experiments several times with different samples, prepared with regard to the crystalline form of kryolite, which, according to M. Descloiseaux, belongs to the triclinic system. As to this last mineral, which has three planes of cleavage perpendicular to one another, I have not succeeded in observing the known lemniscates; under the polarising microscope the plates show the phenomena of polarisation which are proper to crystalline masses.

(To be continued.)

VOLUMETRIC DETERMINATION OF SULPHATES WITHOUT STANDARD SOLUTIONS.

By H. QUANTIN.

THE determination of sulphuric acid as barium sulphate requires minute precautions, none of which can be omitted without inconvenience, and the attempt has therefore been made to substitute for it different volumetric methods. The alkalimetric method proposed by Mohr requires two standard solutions, and a washing of the precipitate which deprives it of every advantage as regards rapidity. The procedures in which a single standard solution of barium chloride is employed are troublesome on account of the frequent trials necessitated by the slow precipitation of the barium sulphate, and there arrives a point when the liquid precipitates equally with barium chloride or with sulphates, a circumstance unfavourable to precision. The most convenient process consists in precipitating the sulphuric acid with a known excess of barium chloride and determining this excess by means of a standard solution of neutral potassium chromate. Here we still require two standard liquids, and the slowness with which the precipitate of barium chromate is deposited renders it difficult to seize the yellow tint which marks the end of the process.

The method about to be described avoids the inconvenience inherent in standard solutions: the determination is effected in a clear liquid and the conclusion is marked by the sensitive reaction of ferrous salts with potassium ferricyanide. The method is based upon the following considerations. If, to a hydrochloric solution of barium chromate we add a solution containing sulphates, the sulphuric acid takes possession of the baryta and sets at liberty an equivalent quantity of chromic acid, which remains combined with the alkali of the sulphate. Now barium chromate is entirely precipitated by a suitable addition of ammonia. If, then, we neutralise with this alkali the solution into which has been introduced the sulphate, barium chromate will be precipitated and there will remain in solution a quantity of alkaline chromate equivalent to the sulphate introduced. If, therefore, we add to equal volumes of the solution of barium chromate, on the one hand, pure potassium sulphate in known quan-

tity, and on the other hand a solution containing sulphates and denoting by p and x the quantities of sulphuric acid brought into play, it is clear that p and x will be proportional to the weight of chromic acid remaining in solution in either case. Hence it results that if we neutralise with ammonia and then bring the two chromic solutions to the same volume, equal fractions of the filtrates will contain quantities of chromic acid proportional to the weights of sulphuric acid precipitated. We may, by the aid of these solutions containing sulphuric acid, peroxidise a solution of iron sulphate, and the volumes n and n_2 of ferrous liquid necessary for the complete reduction of the chromic acid to chromium sesquioxide will be themselves proportional to p and x , whence it results that we have—

$$\frac{p}{x} = \frac{n_1}{n_2}, \text{ whence } x = p \frac{n_2}{n_1}$$

formula which, with correction, becomes—

$$x = p \frac{n_2 - n}{n_1 - n}$$

Preparation of the Solution of Barium Chromate.

Barium chromate dissolves with difficulty in dilute hydrochloric acid; hence it is obtained in the following manner. We make:—1, a solution of neutral potassium chromate containing, per litre, an equivalent of this salt and 100 c.c. of pure hydrochloric acid; 2, a solution of barium chloride containing also an equivalent per litre. The two solutions are mixed in equal volumes, and we filter to separate the barium sulphate, which is sometimes formed in consequence of the presence of potassium sulphate in the chromate. The red liquid thus obtained is that used in the determination, and it must have the following properties:—(1) If neutralised with an excess of ammonia it must yield no precipitate on the subsequent addition of potassium sulphate; 2, if we precipitate 100 c.c. of the solution with ammonia, make up the whole to 1000 c.c., and take 100 c.c. of the clear liquid, not more than 0.2 to 0.5 c.c. of the iron solution should be required to reduce totally the slight excess of chromic acid which it contains; 100 c.c. of this solution precipitate, theoretically, 4.3 grms. potassium sulphate; by reason of the habitual precipitation of barium sulphate prepared at the moment of preparing the liquid, it is well to operate only on 4 grms. potassium sulphate. If it were necessary we might add to the solution a suitable quantity of barium chloride and potassium chromate, so that the liquid precipitated by the ammonia should always contain a trace of alkaline chromate and never of barium. The variations which may occur further in the composition of the liquid are of no importance, since it is not titrated in the strict sense of the term.

Manner of Operating.

Into a flask marked at 1000 c.c. we introduce successively 500 to 600 c.c. of distilled water and 4 grms. of pure potassium sulphate containing $p = x$ of sulphuric acid. When dissolved we introduce by means of a pipette 100 c.c. of the solution of barium chromate and agitate for ten minutes, and then neutralise with an excess of ammonia very free from sulphate. After the precipitate has settled the liquid ought to be yellow and never reddish (arising from an insufficiency of ammonia). It is agitated afresh and made up to 1000 c.c. After having carefully ascertained that the mixed liquid is homogeneous it is carefully filtered through Swedish paper so as to obtain a liquid absolutely limpid. It is ascertained by testing a fraction of the liquid previously acidulated with hydrochloric acid, that all the sulphate has been precipitated; 100 c.c. are then taken for determination and mixed with 10 c.c. of pure sulphuric acid, of full strength. The iron liquor is then poured in by means of a graduated burette which can contain 35 c.c. The original red tint of the solution becomes brownish, green, and finally a bluish green. It is only when every trace of yellow has dis-

appeared that we proceed to the spotting-tests. These are performed in the following manner:—The liquid being energetically stirred up by means of an agitator so as to thoroughly mix all the layers, we take a drop of the solution at the end of another rod, which must not be plunged into the liquid above 1 c.m. at most. The drop is then placed upon a drop of potassium ferricyanide, which is deposited beforehand upon a greased plate. The operation is completed, when a light blue tint appears, which must be distinct, but not deep. The solution of ferricyanide must be fresh, and so dilute that the drops appear colourless, and it must not be turned blue by ferric salts. A suitable solution is readily obtained by passing a current of chlorine into a solution of commercial ferricyanide, and expelling the excess of chlorine by boiling.

We then operate in exactly the same manner upon the solution of the sulphates to be analysed.

Before each series of determinations we determine the correction necessitated by the presence in the chromic liquid of a slight excess of chromate by introducing into a flask marked at 1000 c.c., 100 c.c. of the solution of barium chromate, precipitating with ammonia, making up to 1000 c.c., filtering, and proceeding as above. If the value found for n (referred to pure potassium sulphate) has changed little since the foregoing operations, it is useless to re-determine the correction n . We have thus to effect $p+1$ operations for p determinations. An hour suffices for completing three or four analyses. The method just described supposes that the substance submitted to analysis contains merely bodies which do not precipitate barium chloride and give no coloured reaction with ferricyanide. All cases may be brought to the above by operating as follows:—We weigh out 8 grms. of the substance, which are then dissolved in a minimum of hot water. We add a slight excess of ammonia, which precipitates the metallic oxides, which are afterwards re-dissolved in a little nitric acid containing ferric nitrate. The solution is again precipitated by ammonia, adding a little sodium carbonate (excess of which must be carefully avoided), and the liquid is evaporated to dryness; at about 300° all the oxides proper, such as iron and alumina, along with silica and phosphoric acid, are rendered insoluble; the organic matters, if any, are destroyed, and the presence of sodium carbonate prevents the sulphuric acid of the ammonium sulphate from disappearing if the evaporation to dryness has been carried beyond 300°. The insoluble portion is then treated with boiling water and the whole introduced into a flask marked at 250 c.c.; it is filtered and 125 c.c. are taken for analysis, that is, 4 grms. of the original substance. If the volume occupied by the insoluble portion is worth notice, it may be taken into account with 0.2 c.c. by collecting it on a filter without washing, and determining its volume after desiccation. This determination can be easily made with an approximation of 0.2 c.c. by introducing the precipitate into a flask containing 50 c.c. and making the volume up to the mark by pouring in distilled water from a burette.

Conditions of the Accuracy of the Method.

The iron-liquor, though not standardised, should present an approximate degree of concentration, as derived from the formula—

$$x = p \frac{n_2 - n}{n_1 - n}$$

n being the correction. This formula shows, in fact, that the errors being necessarily in the same direction in n , n_1 , and n_2 , the introduction of a subtractive correction reduces the error in reading off the burettes, since this correction bears upon both terms of the fraction. The error in reading off being, at the utmost, 0.1 c.c., the precision will be so much the greater the more considerable are the terms of the fraction, that is, the smaller is n in proportion to $n_2 - n$ and $n_1 - n$. Now $n_1 - n$ increases with p , since the quantity of chromic acid remaining in solution increases with the weight p of sulphuric acid precipitated.

To reconcile these conditions of accuracy with the use of burettes, a concentrated solution of ferrous sulphate should be diluted so that $n_2 - n$ and $n_1 - n$ may be comprised between 20 and 35 c.c.

A sulphate mixed with salts of iron, aluminium, and copper yielded, on analysis, 25.3 per cent sulphuric acid in place of 25.5; the same mixed with sodium chloride and nitrate in large excess gave 25.6. The discrepancy between the results given by the volumetric method just described has never exceeded 0.5 per cent in sulphates containing 40 to 60 per cent of sulphuric acid, and it cannot be said that either of these results is preferable to the other.—*Moniteur Scientifique*, Quesneville (October, 1886, p. 1222).

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 224.)

Titration of the Uranium Solution.

THE titration of the uranium solution is accomplished as follows:—

Standardising the Solution of Uranium.—Pour out in a flask (marked at 75 c.c.) 10 c.c. of standard phosphoric acid solution, measured by means of an accurate pipette, add 5 c.c. of the acid acetate of soda and distilled water to make about 30 c.c., and heat to the boiling-point. Then titrate by running the solution of uranium into the flask by means of a graduated burette, stirring after each addition, and testing the liquid, to the tenth, with some drops of ferrocyanide of potassium placed upon a greased dish. As the quantity of solution of uranium ought to be very near 10 c.c., first add about 9 c.c. without trial. Continue with two or three drops each time, until the test indicates the end of the operation.

When you observe in the last trial a sensible change of colour, refill the glass to the mark with boiling distilled water, and make a new trial. If in the first part of the operation the point of saturation has not been passed, it is generally necessary to add a drop or two of uranium solution, in order to obtain the characteristic red colour, a quantity rendered necessary by the increase of the quantity of the liquor.

This method of procedure permits one to obtain great precision the second time, whereas at first one perceives the point of saturation a little before it has really been obtained.

It is evident that the results obtained are not absolutely exact, for it has been necessary to add not only enough of the uranium solution to exactly precipitate the phosphoric acid, but also enough to give the colouration with the cyanide.

This quantity, however, can be exactly determined, since the same quantity of solution, viz. 75 c.c., is used for every determination, by making some blank determinations, i.e., without any phosphates being present. The amount of uranium solution necessary to give the colouration to the ferrocyanide having been determined, it is thereafter accounted for in the titrations. The exact method of making this determination is as follows:—

The manipulation is made as in the preceding case: Into a flat-bottomed Bohemian flask of about 150 c.c. capacity, and marked at 75 c.c.; pour, by means of a pipette, 5 c.c. solution of acetate of soda; add warm distilled water, almost to the mark, and place the flask upon a sand bath heated with gas or otherwise, and carry to the boiling-point. Take it off the fire, complete the volume to 75 c.c. with a little distilled warm water, and pour in the glass one or two drops of the solution of uranium by means of a graduated burette which has been previously filled to zero. After each drop of the solution of uranium,

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

stir and try the liquid upon a drop of ferrocyanide of potassium, as has been previously indicated. For an experienced eye generally four to six drops are necessary in order to obtain the characteristic colouration—i.e., 0.2 to 0.3 c.c. Beginners often use 0.5 to 0.6 c.c., and even more.

The only important point is to stop as soon as one certainly sees a red tint, for afterwards the intensity of the colour is not increased proportionally to the quantity of the liquor employed.

In the preceding operations three causes of error must be avoided.

The first is the error which may arise from the colouration imparted to the drop of ferrocyanide of potassium from the small quantity of solution removed by the stirring-rod when the eye is not sufficiently experienced.

It is very easy to determine when the end of the reaction has been reached. In order to do this, note the quantity of solution of uranium already employed and add to it four drops; stir and make a new trial upon a drop of ferrocyanide of potassium near the preceding. If the red tint does not clearly appear on taking away the rod it is fair to conclude that it was a mistake, and continue the trial. If, on the contrary, the colour appears clearly, the obtained number is taken as correct. It is always well to end the trial by this proof of four supplementary drops, which exaggerate the colour and confirm the number found.

The second cause of error, and that which, moreover, is most frequent, consists in overreaching the end of the reaction by operating too quickly. In place of giving a colour scarcely perceptible, the trial upon the ferrocyanide gives them a very marked colouration.

In this case the analysis can yet be saved.

There must be in this case a decimal liquor prepared with 100 c.c. of standard phosphoric acid solution diluted to a litre with distilled water. Add to the assay 10 c.c. of this decimal liquor and continue the titration. Account must be taken in the calculation of the quantity of phosphoric acid added.

Finally, the third cause of error is in the froth, which is often produced upon the liquid by stirring. It may retain a portion of the solution of uranium which falls on its surface and prevent its mixture with the remainder of the liquid.

If the glass rod touches this foam charged with uranium, the characteristic colour is obtained before the real saturation. It is consequently necessary to avoid, as much as possible, the formation of the foam, and above all to have a care to take the drop of the sample, after stirring, only in the middle of the liquid where the foam does not exist.

Titration of the Phosphate in the Sample of Fertilisers.

In this case, the quantity of phosphate being unknown, it is necessary to proceed slowly, so as not to pass the point of saturation. Since, in this first attempt, a certain error must be introduced by the drops taken out for trial, the result must not be regarded as final. For the second determination, however, almost the entire quantity of reagent can be added at once, and this source of error avoided. All samples should be treated in duplicate. The committee conclude this part of their report with the following observations:—

This method of analysis, much longer to describe than to execute, gives results perfectly exact and always concordant, when it is well managed provided the titrated liquors, upon which reliance is placed, are prepared exactly and frequently verified, as we have indicated.

The standard uranium solution ought to be verified and rectified every three or four days. That of the standard phosphoric acid ought to be tested each time that the temperature of the laboratory undergoes an important change. A solution prepared, for example, in winter, when the temperature of the laboratory is from 15 to 18°, will not be exact in summer, when the temperature is 28

to 30°, at least if care be not taken to cool it before taking the necessary quantities.

The report closes with a very brief description of the methods to be used for estimating soluble and reverted phosphoric acid. These methods, especially for reverted acid, are entirely different from those recommended by our committee. As will be seen, the citrate of ammonium solution is made strongly alkaline, and the precipitation of the phosphoric acid is accomplished with a magnesia mixture in the presence of the citrate. In my opinion the method which is given below is far inferior to the procedure which has been adopted by our committee.

Preparation of the Sample for Analysis.—The sample sent to an expert chemist is prepared as we have already indicated in the previous pages; that is to say, it is poured in a sieve of which the meshes are 1 m.m. apart, and sifted upon a sheet of white paper. The parts which do not pass through are broken with the hand, or in a mortar, and added to the first portions. The product, well mixed, is introduced into a flask. In this state the mass presents all the homogeneity necessary for analysis. Some fertilisers are sticky, and in this state cannot be sifted. It is necessary, in this case, to mix them with their own weight of sulphate of lime precipitated and dried at 160°, or sand of Fontainebleau, washed with hydrochloric acid and dried, which divides them perfectly and permits them to be worked through the meshes of the sieve.

Extraction of the Products Soluble in Distilled Water.—The products being prepared as has been said, weigh from 1 to 5 grms., and put in the bottom of a glass mortar. Add 20 c.c. of distilled water, mix gently, and, after a minute, decant the part floating upon the surface into a little funnel furnished with a filter, and placed in a graduated flask of 150 c.c. This operation is renewed three times, and is terminated by an intimate mixture of the material with the distilled water. When the volume of the filtrate is about 100 c.c. the remainder is poured upon the filter and the washing continued to make the volume to 150 c.c. Stir to render the solution homogeneous, and transfer to a beaker of 300 grms. capacity.

Solution of Retrograde Phosphates with Citrate of Ammonia.—The filter is taken from the funnel, and is introduced into a graduated flask of 150 c.c. capacity with 60 c.c. of alkaline ammonia citrate prepared in the following way:—

Pure citric acid	Grms. 400
Ammonia (22°)	C.c. 500

Pour the ammonia on the citric acid in crystals in a large capsule. The mass is heated and the solution takes place rapidly. When this is complete and cool, pour it into a graduated flask of 1 litre capacity and refill just to the mark with ammonia at 22°. It is preserved for use in a well-stoppered flask. This solution ought to be strongly alkaline.

The flask in which the filter and citrate of ammonia are put is stoppered and violently shaken to disintegrate the filter and bring into suspension the reverted phosphates. Add about 60 c.c. of distilled water, shake, and set aside for twelve hours at least, and twenty-four hours at most. Complete the volume to 150 c.c. with distilled water, and, after mixing, filter.

Precipitation.—Two solutions have now been obtained which can be precipitated together or separately, according to what is desired.

The most ordinary process is to mix quantities of 25, 50, or 100 c.c., representing 0.25, 0.50, or 1 grm. of material, according to the presumed value, in a beaker with 10 to 20 c.c. of magnesia solution made as follows:—

Carbonate of magnesia	Grms. 50
Chloride of ammonium	100
Water	100
Hydrochloric acid	C.c. 120

Dissolve and add—

Ammonia (22°)	C.c. 100
Distilled water	..	Q.S. to make 1 litre.

Add an excess of ammonia, and leave for twelve hours under a bell glass. The phosphoric acid contained in the liquid separates in a state of ammonio-magnesian phosphate. Gather it upon a little filter, wash it with ammonia water, re-dissolve and titrate it with the solution of uranium as previously directed.

In respect of this method, employed universally in France and Belgium, Mohr (*Chem. Zeit.*, 1886, No. 44, p. 675) makes the following observations:—The direct precipitation by magnesia of phosphoric acid dissolved in citrate of ammonia is employed as a standard method in Belgium and France. As a result of this process it is no unusual thing to find the French analyses falling from 1 to 3 per cent behind the German. He especially condemns the habit of estimating the soluble and reverted forms of the acid at a single operation. By first removing the soluble and afterward using a much less quantity of the citrate very good results are obtained. The analyses should be made as follows:—

Two grms. of the superphosphate are rubbed in a mortar with warm water and treated with a proper quantity of acetate of soda. The phosphates of iron and alumina thus produced remain with the residue in filtration. The soluble P_2O_5 is now washed out and the filtrate made up to 200 c.c. The estimation is then made in an aliquot part, 50 c.c., in the usual way. The residue is digested with an alkaline solution of citrate of ammonia for an hour at 40° to 50° C., filtered, and the P_2O_5 precipitated directly with the magnesia mixture.

In other parts of Europe we may also find associations of official chemists engaged largely in the same kind of work which occupies us here.

Chief among these bodies must be named the English Society of Public Analysts. In this society are discussed all the problems relating to the duties of public analysts, and the methods employed in analytical work receive a large share of attention. In illustration of this I may call attention to the discussion of the method of milk analysis, which has occupied so large an amount of time of the society during the past two years. As a result of this work the old methods of estimating fat in milk have been entirely superseded. The society has formally adopted the principle of Adams, which is based on a preliminary absorption of the milk by bibulous paper, and after drying rolling the paper into a coil suitable for insertion in a syphon extractor. Blotting-paper was first proposed by Adams for this purpose, but Johnstone subsequently recommended the use of thick blotting-paper, and this seems to be as successful as the first method. I have had the method partially tried in the laboratory here and with pleasing results. The filtering paper, previously thoroughly extracted with ether, is cut into strips $2\frac{1}{2}$ inches wide and 2 feet long. Five c.c. of milk from a weighing bottle are dropped along the central portion of this slip of paper, being careful to leave the ends, and, if possible, a narrow margin along the sides, dry. The paper is then hung up over a sand bath or other hot place, where it becomes entirely dry in a very few minutes. It is then rolled into a coil and placed in a syphon extractor.

English analysts have found that this method gives fully 2 per cent more fat in an ordinary rich milk than in any of the old processes of evaporation of the milk with sand or gypsum.

I only mention the above to give an idea of the kind of work which is accomplished by this society, and which is so entirely in the line of our own investigations.

In Germany there are numerous societies having in general the same object in view. One of these in Bavaria has lately issued two valuable bulletins which show the general character of the work done. This society had various committees appointed for the purpose of considering different subjects. For instance, there were committees for the investigation of the methods of analysis of milk, beer, wine, drinking-water, flour and bread, butter and butter substitutes, tea, coffee, and chocolate productions, &c. All of these committees made reports at the annual

meetings, and these with the discussions thereon were printed in the bulletins. In the matter of milk analysis to compare the work of the Bavarian society with that of English, the committee adopted a report which covers 114 closely printed pages. All the usual methods of analysis are carefully discussed, and the preference given finally to Soxhlet's areometric method. At the time the report was made, however, it is necessary to state that the committee had not seen the recent work of the English society to which I have alluded, and therefore made no recommendation in respect of the tables which are used for the computation of Soxhlet's method, and which are based on the old methods of the gravimetric determination of fat. It is evident, however, that if the results obtained by the English analysts should prove to be true, it will be necessary to make a careful revision of this table in order to reach accurate results by the Soxhlet method.

Having thus briefly called attention to some of the work which is carried on by societies in other parts of the world, having in general the same object in view as our own, it may be proper to remind you that the scope of our own society appears somewhat limited as compared with those mentioned. It seems to me that our numbers might be materially increased and the good results of our meetings widely extended if our investigations were made to include a wider range of subjects. Every problem connected with chemical agricultural analysis falling within the range of the studies of any one connected officially with the agricultural interests of the country seems to me to be a proper theme for our discussion here. Thus all the problems relating to the adulteration of food, the general method of agricultural analysis, and all other matters which concern, in common, the analyst and the public, could be included among the duties and privileges of this body. In this way large numbers of chemists in official and semi-official life who do not feel that they are properly candidates for membership in our body could be added to our numbers. In consideration of these facts I suggest whether it might not be advisable to appoint a committee to consider the propriety of revising that clause of our constitution which limits our membership and the scope of our investigations.

(To be continued).

CORRESPONDENCE.

CONTACT-ACTION VERSUS CONDENSATION.

To the Editor of the Chemical News.

SIR,—Will you kindly allow me a small portion of space to suggest to Mr. Blunt (see CHEM. NEWS, vol. liv., p. 212) that he appears to have missed the drift of the paper to which he refers?

1. The oxidation of "ignoble" metals as a consequence of absorption of atmospheric oxygen belongs clearly to quite a different category of phenomena.

2. The condensation of gases in porous bodies (*e.g.*, of ammonia in charcoal) at ordinary temperatures is a fact so well known, and so often illustrated experimentally wherever chemistry is really taught, that I felt justified in taking it for granted. If Mr. Blunt, however, will reverse his experiment and heat the charcoal, after it has been carried on the mercury to the top of the tube, he will soon see that *the application of heat does not promote condensation*. Yet it is just this elevation of temperature, in the cases cited by me in the paper, which renders contact-action effective in inducing chemical action between gases which do not act upon one another under ordinary conditions.—I am, &c.,

A. IRVING.

Wellington College, Berks
October 24, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 16, October 18, 1886.

Researches on the Tension of Dry Ammonium Bicarbonate.—MM. Berthelot and André.—The part played by the three components of the ammoniacal salt is not the same in its dissociation, carbonic acid and gaseous ammonia, even in great excess, not having a sensible influence upon the tension of the bicarbonate at the ordinary temperature, whilst liquid water determines its decomposition, independently of the laws of dissociation of the salt, properly speaking, and probably in the ratio of its particular combinations with the salt or with its components.

Analysis of a Cosmic Dust which fell on the Andes near San Fernando, in Chili.—E. Nordenskiöld.—The dust in question was collected in November, 1883, after a red cloud had been seen high over the summits. The mountains were, at the time, covered with fresh-fallen snow, and the weather both in Chili and in the La Plata countries had been very wet. The dust consisted chiefly of ferric oxide, nickel oxide with traces of cobaltous oxide, silica, and magnesia. The author is of opinion that it is neither a product of the Krakatoa eruption nor a terrestrial dust.

On Certain Pyridic Bases.—A. Ladenburg.—The author has obtained synthetically a number of bases of the pyridic series, including α , β , and γ -methylpyridin, $\alpha\alpha$ -dimethylpyridin, $\alpha\gamma$ -dimethylpyridin, α -ethylpyridin, γ -ethylpyridin, $\alpha\gamma$ -diethylpyridin, and α and χ -isopropylpyridin.

Constant Presence of Microbia in the Waters of Luchon, collected at the Temperature of 64°, and on their Action in the Production of Baregine.—A. Certes and Garrigon.—The water taken at its highest temperature, and the sediments deposited at the bottom and along the margins of the tank, contain small movable rods, very transparent and difficult to observe. There are also a few longer and motionless filaments. Neither the one nor the other were accompanied by granulations of reduced sulphur. No algæ, confervæ, diatoms, nor living infusoria were present. Going further from the spring as the water cooled, both the rod-organisms and the filaments multiplied. Then only, and at temperatures not exceeding 50°, there appear those masses of baregine which are the zooglae of the rods mixed with grains of reduced sulphur.

Biedermann's Central Blatt fur Agrikultur Chemie.
Vol. xv., Part 6.

The Oxidation of Ammonia in Waters and Soils.—J. Uffelman.—The author proves that the oxidation of ammonia can take place without the co-operation of microbia, at least in cases of strong surface attraction. Experiments with spring water, and with the water of the Rostock town supply, showed that even in water not free from germs, and in vessels not sterilised, the oxidation of ammonia takes place much more slowly than it is commonly assumed.

Formation of Saltpetre Earths in the Tropics.—A. Muntz and V. Marciano.—From the *Comptes Rendus*.

Physiological Behaviour of Benzoic-Sulphinid (Saccharine).—A. Mosso, H. Mosso, and V. Aducco.—Saccharine introduced into the animal organism is eliminated unchanged in the urine, without producing any effect.

Conditions of the Development and the Activity of Chlorophyll.—Prof. J. H. Gilbert.—From the *Gardener's Chronicle*.

Chlorophyll and the Reduction of Carbonic Acid by Vegetation.—C. Timiriazeff.—From the *Comptes Rendus*.

Certain Conditions of the Development and Activity of Chlorophyll.—Prof. J. H. Gilbert.—From the *CHEMICAL NEWS*.

The Respiration of Leaves in Darkness.—P. Dehérain and L. Maquenne.—During respiration nitrogen is neither liberated nor absorbed. The ratio $\frac{CO_2}{O}$ is independent of the time spent by the plant in darkness. This relation within very wide limits, is independent of the partial pressure of oxygen or of carbonic acid in the ambient atmosphere. The real value of $\frac{CO_2}{O}$ increases with the temperature.

The Occurrence of the Constituents of Milk-Sugar in Plants.—A. Muntz.—From the *Comptes Rendus*.

Composition of Certain Nectars.—A. von Planta.—The nectar of *Protea mellifera* contains 73.17 per cent of dry matter, of which 70.08 consist of glucose and 1.31 of cane sugar. That of *Hoya carnosa* contains 35.65 per cent cane-sugar and 4.99 glycerin. The nectar of *Bignonia radicans* contains 14.84 glucose and 0.437 cane-sugar. Old samples of honey contain from 17 to 25 per cent of moisture, and recent samples from 20 to 33, the latter figure only in one case.

Researches on the Proportion and the Increase of Dry Matters, and of Chemical Constituents in Sinapis alba.—Dr. E. Hornberger.

Composition of White Mustard (Sinapis alba) at Different Stages of Vegetation.—Dr. Troschke.—These two papers do not admit of useful abstraction.

Cultivation of Leguminous Crops.—Beck-Antoine.—The author recommends, from his own experience, the cultivation of leguminous plants on sandy soils.

Culture Experiments with Different Sorts of Oats.—Prof. Kühn, Dr. Schwab, and Administrator Menzel.—This paper is of no chemical interest.

The Proportions of Starch and Sugar in Tobacco-Leaves during Ripening and Drying.—Hermann Müller.—The author has studied the occurrence of starch in fermented tobacco-leaves, that of starch in ripening tobacco-leaves, and the behaviour of the carbohydrates on drying.

The Mosaic Disease of Tobacco.—Dr. Adolf Mayer.—The author finds that this affection is of bacterial character, and is decidedly infectious. He makes the curious statement that "the disease has hitherto been only known in England," though tobacco is not cultivated here.

Methods of Butter Analysis.—H. B. Cornwall.—From the *CHEMICAL NEWS*.

The Production of Maltose and of Maltose Syrup.—A description of two patents, the one taken out by P. Leplay and A. Cuisinier, and the other by the Société Anonyme Générale de Maltose.

The Formation of Alkaloids by the Action of Ammonia upon Glucose.—C. Tanret.—From the *Comptes Rendus*.

Journal de Pharmacie et de Chimie.
Vol. xiv., No. 6, September 15, 1886.

Constitution of Pilocarpine.—MM. Hardy and Calmels.—According to the authors there exists in pilocarpine only one lateral chain in the β position opposite to the pyridic nucleus; pyridine is substituted in the α position in this chain; the chain constitutes a lactic

group, and the pilocarpine becomes the trimethyl-betaine corresponding to this acid.

The Hammam Salahine.—Julien Girard.—An account of a hot saline spring in North Africa.

Combinations of Chloral and Resorcine.—H. Causse.—In the action of chloral upon resorcine in presence of dilute sulphuric acid there are formed two series of products; the one crystalline, derived from a molecular combination, corresponding to an alcoholate, and the other amorphous, representing a combination of a polymer of chloral with a polymer of resorcine.

Artificial Colouration of Cheese.—MM. Frehse and Tissot.—The aniline yellows now used for this purpose may be extracted by means of methylic alcohol, and two solutions subjected to examination. Ethylic alcohol extracts along with the colour certain impurities which interfere with the reactions.

On Lantanine.—M. Buiza.—This base, discovered by Negrete, is obtained from a Brazilian plant belonging to the family of the *Verbenaceæ*. The composition and reactions are not given.

Reaction of Tin.—M. Bassett.—From the CHEMICAL NEWS.

On Chelidonic Acid.—M. Ernest Schmidt.—The author proves that the acid of *Chelidonium majus* is absolutely identical with succinic acid.

Presence of Vanilline in Assafœtida.—M. Ern.—Very small quantities of vanilline can be extracted from this drug.

Composition of certain kinds of Nectar.—A. Von Planta.—Already noticed.

The Action of Caffeine.—A. Langgaard.—The author finds that caffeine is to a certain extent an antidote to curare and similar poisons. It has also the same action with respect to conicine and the poison of mussels.

Ptomaine Extracted from a Poisonous Cheese.—V. C. Vaughan.—A notice of the symptoms produced by the ingestion of tyrotoxin.

MISCELLANEOUS.

The Manchester Jubilee Exhibition, 1887.—We understand that it has been decided that the time during which applications for space can be received from intending exhibitors shall be extended to December 1st.

Exhibition of Rare Chemicals.—At the last meeting of the Society of German Naturalists a large number of chemical compounds were exhibited by Dr. Theodor Schuchardt, of Görlitz. They were principally organic compounds, but among the inorganic exhibits we note some of the rare metals, such as tellurium, gallium (fused and crystalline), indium, and germanium, and some of their rarer salts.

Paste for Labelling.—L. Eliel.—1. Tragacanth 1 oz., gum arabic 4 ozs., water 1 pint; dissolve, strain, and add thymol 14 grains, glycerin 4 ozs., and water to make 2 pints. Shake or stir before using it.

2. Rye flour 4 ozs., alum $\frac{1}{2}$ oz., water 8 ozs.; rub to a smooth paste, pour into a pint of boiling water, heat until thick, and finally add glycerin 1 oz., and oil of cloves 30 drops.

3. Rye flour 4 ozs., water 1 pint; mix, strain, add nitric acid 1 drachm, heat until thickened, and finally add carbolic acid 10 minims, oil of cloves 10 minims, and glycerin 1 oz.

4. Dextrin 8 parts, water 10 parts, acetic acid 2 parts; mix to a smooth paste and add alcohol 2 parts. This is suitable for bottles or wood, but not for tin, for which the first three are likewise adapted.

A paste very similar to 3, but omitting nitric acid and glycerin, is also recommended by Dr. H. T. Cummings. —*Am. Journ. Pharmacy.*

Pathogenic Organisms in Water.—At the meeting of the Bavarian Association for Applied Chemistry (August 6th and 7th, 1886) Dr. Emmerich stated that pathogenic organisms quickly perish in water; only in a single case had Wolffhügel observed a longer permanence. His experiments were made at 22° and 35°, and no one drinks water at such temperatures. On the introduction of pathogenic microbes into drinking water, the struggle between them and the microbes inhabiting the water is always decided in favour of the latter. On a slip the typhus bacilli prevail, but in water the water-bacilli predominate. The bacteriological examination of water is only of secondary importance. In ordinary water there occur many organisms which form colonies resembling those of the typhus bacilli, but possess a smell like herrings, whilst the colonies of typhus bacilli have a nutty smell.—*Chemiker Zeitung.*

German Congress of Naturalists and Physicians.—At a recent meeting Dr. Plagge read a memoir on the Filtration of Water, in which he argued that the essential task of filtration is to free water from infectious matters. As such matter consists chiefly of bacteria, the value of a filter must be judged according to its efficacy in the destruction or removal of the bacteria present in the water. The distinction of the bacteria into pathogenous and non-pathogenous is here unimportant, since a filter which allows the non-pathogenous germs to pass will not keep back those which are pathogenous, whilst, on the other hand, we are justified in assuming that a filter which keeps back all other bacteria will give protection against infectious matters. Most of the ordinary domestic filters, and especially those containing as their material spongy iron, carbon, stone, gravel, and cellulose, do not—according to the author's observations—come up to the above requirement. On the contrary, there is generally found a marked increase of organisms in the filtering material. Experiments made with pure cultures of typhus and cholera prove that such filters allow these infectious matters to pass without hindrance. Better results were obtained with clay and asbestos filters of different constructions (Chamberland, Breyer, Olschewsky, Arnold, and Schirmer), as for a certain time they yielded water perfectly free from germs. However, it was not found practicable with any of these apparatus to obtain water perfectly free from microbes. According to Hesse, asbestos strongly compressed, and especially dense cells of clay, form a filtering material which yields water permanently germ-free. On this point the author is for the present unable to decide, since these apparatus have not been produced for practice, and he has not been able to procure such.—*Chemiker Zeitung.*

MEETINGS FOR THE WEEK.

WEDNESDAY, 10th.—Society of Public Analysts, 8. "On the Density and some other Characters of Waxes and Allied Bodies," by Alfred H. Allen, F.C.S.
"On the Conversion of Starch into Glucose by means of Hydrochloric Acid," by Sidney Harvey, F.C.S.

SATURDAY, 12th.—Physical, 3. "Note on the Internal Resistance of Thermometers," by Mr. A. W. Clayden. "On the Peculiar Sunrise Shadows of Adam's Peak in Ceylon," by the Hon. Ralph Abercromby.

ERRATUM.—P. 225, col. 1, line 19 from top. for "Ostindioch" read "Ostindisch."

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London: J. and A. CHURCHILL, 11, New Burlington Street.

THE CHEMICAL NEWS.

VOL. LIV. No. 1407.

SIMPLE OR COMPOUND?

It is by no means an occurrence without precedent for two minds to arrive almost simultaneously at conclusions very nearly identical. Of such coincidences the present season has just furnished a striking example. A paper by Prof. A. E. Nordenskiöld, read before the French Academy of Sciences on November 2nd, a translation of which will be found in the CHEMICAL NEWS of to-day, repeats the suggestion which formed, so to speak, the key-note of the address delivered by Mr. Crookes before the Chemical Section of the British Association in September last. This coincidence, it need scarcely be said, is of no small value. It shows us that an idea thus occurring almost simultaneously to two investigators not working in concert may claim a higher rank than that of a day-dream.

Professor Nordenskiöld's paper discusses the atomic weight of the oxide of gadolinium, a name which he has given—somewhat unfortunately we think—to the crude earths, yttria, erbia, ytterbia, &c., contained in gadolinite and similar minerals. We say *unfortunately* because it will be remembered that the name gadolinium has already been appropriated by M. de Mariguac for the metal of his Ya.

Upon this mixture of earths! the distinguished Swedish *savant* has been working for some time. By well-known methods he resolves it into three elements, yttrium, erbium, and ytterbium, always in association together. We may remark parenthetically that in addition to the above-mentioned "elements"—a term which we use not without diffidence—there are almost certainly present thulium, holmium, terbium (?), and one or two more unnamed bodies. This, however, only presents the argument of Prof. Nordenskiöld with greater force.

Mr. Crookes said in the Birmingham address: "From every chemical point of view the stable molecular group yttrium" (in the older sense of the term) "behaves as an element." And what is the opinion of Prof. Nordenskiöld? "That oxide of gadolinium, although it is not the oxide of a simple body, but a mixture of three isomorphous oxides, even when it is derived from totally different minerals found in localities far apart from one another, possesses a constant atomic weight." Surely the possession of a constant atomic weight is one of the most characteristic features of a so-called simple body.

But Mr. Crookes goes further. He says: "And as this is the case with one element, it is probably so in a greater or less degree with all." And again: "When we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on." Further we read: "The minerals of the class of samarskite and gadolinite may be regarded as the cosmical lumber room where the elements in a state of arrested development—the unconnected missing links of inorganic Darwinism—are finally aggregated."

There is another coincidence here too important to be overlooked. Prof. Nordenskiöld, in the concluding sentence of his memoir, says: "It seems that chemists here find themselves face to face with a problem analogous to that presented to astronomers in the origin of the minor planets." Now in the Birmingham address we find that Mr. Crookes had used the very same figure: "Others—the asteroids among the elements—have come into being and have survived, but only on a limited scale."

If we now sum up and generalise the teachings of

Prof. Nordenskiöld as laid down in the memoir in question, we can scarcely help seeing that he calls in question the current dogma of the elements of modern chemistry as bodies absolutely simple, different in kind from all compounds and primordial, either independently created or self-existent. He evidently conceives of them as having originated. No less evidently does he question their absolute simplicity when he speaks of "substances of a kind that chemists as yet are forced to regard as elements."

In short, though not going as far as Mr. Crookes, though not suggesting any scheme for the genesis of the elements, Prof. Nordenskiöld may be considered as having given in his substantial adhesion to the principles laid down in the Birmingham address. Had this adhesion been concious on his part, following upon a study of the address, it would still have been of great value. But though writing about two months subsequently to the meeting of the British Association he does not appear ever to have come in contact with Mr. Crookes's speech, but to have been led to views so closely similar by an independent study of the "rare earths." It need not be demonstrated that this circumstance greatly enhances the weight of his support, and is an authoritative confirmation of the advice given by Mr. Crookes to young chemists at the close of his address.

ON THE RELATIVE STABILITY OF THE MONO-HYDROCHLORIDES, $C_{10}H_{17}Cl$,

OBTAINED FROM

TURPENTINE AND CAMPHENE RESPECTIVELY.*

By ERNEST F. EHRHARDT,
Tangye Scholar, Mason College, Birmingham.

IN 1873 Riban showed (*Chem. Soc. Journ.*, xxvii., p. 154) that the isomeric compounds, $C_{10}H_{17}Cl$, might be distinguished from one another by the differences in their behaviour when acted on by water. Terpene hydrochloride is not decomposed by cold water, and only slightly at 100°. Camphene hydrochlorides are slowly decomposed by cold water, and readily at 100°, the crystalline camphene being regenerated.

Early in this year I was led by Dr. Tilden to examine these two compounds, to see whether their dissociation under the influence of heat bore any relation to the rate of decomposition by water.

To measure the dissociation the vapour density was determined at different temperatures.

Terpene hydrochloride was prepared by saturating re-distilled American turpentine oil (boiling-point 156° to 160°) with hydrochloric acid gas, keeping the liquid cold. The hydrochloride was drained and re-crystallised once from alcohol, and then dried first by exposure to air, then under a bell-glass over quicklime.

The vapour densities were in both cases determined by Victor Meyer's method, using a bath of Colza oil.

The density of the terpene hydrochloride was determined at temperatures ranging from 223° to 263°.

(I.) $w = 0.1336$. Temperature of oil-bath = 225°. $v = 21.0$ c.c. $t = 19^\circ$. $P = 730$ m.m.
Vapour density = 80.9.

(II.) $w = 0.1428$. Temperature = 223°. $v = 22.0$ c.c. $t = 17.3^\circ$. $P = 724.7$ m.m.
Vapour density = 80.8.
Means.—Temperature = 224°. Vapour density = 80.85.

(III.) $w = 0.1157$. Temperature = 233.4°. $v = 17.78$ c.c. $t = 14^\circ$. $P = 725.45$ m.m.
Vapour density = 80.0.

* A Paper read before the British Association, Birmingham Meeting, Section B.

- (IV.) $w = 0.1314$. Temperature 233.5° to 234.5° .
 $v = 20.20$ c.c. $t = 10.2^{\circ}$. $P = 722.3$ m.m.
Vapour density $= 79.25$.
- (V.) $w = 0.1418$. Temperature $= 233.5^{\circ}$ to 235° .
 $v = 22.50$ c.c. $t = 14^{\circ}$. $P = 718.7$ m.m.
Vapour density $= 78.25$.
Means.—Temperature $= 233.9^{\circ}$.
Vapour density $= 79.15$.
- (VI.) $w = 0.1308$. Temperature $= 240^{\circ}$ to 242° .
 $v = 21.23$ c.c. $t = 12.8^{\circ}$. $P = 717.78$ m.m.
Vapour density $= 76.22$.
- (VII.) $w = 0.1088$. Temperature $= 250^{\circ}$ to 251.5° .
 $v = 19.42$ c.c. $t = 12^{\circ}$. $P = 711.0$ m.m.
Vapour density $= 69.77$.
- (VIII.) $w = 0.0964$. Temperature $= 262^{\circ}$ to 263° .
 $v = 20.75$ c.c. $t = 12.8^{\circ}$. $P = 733.63$ m.m.
Vapour density $= 56.23$.

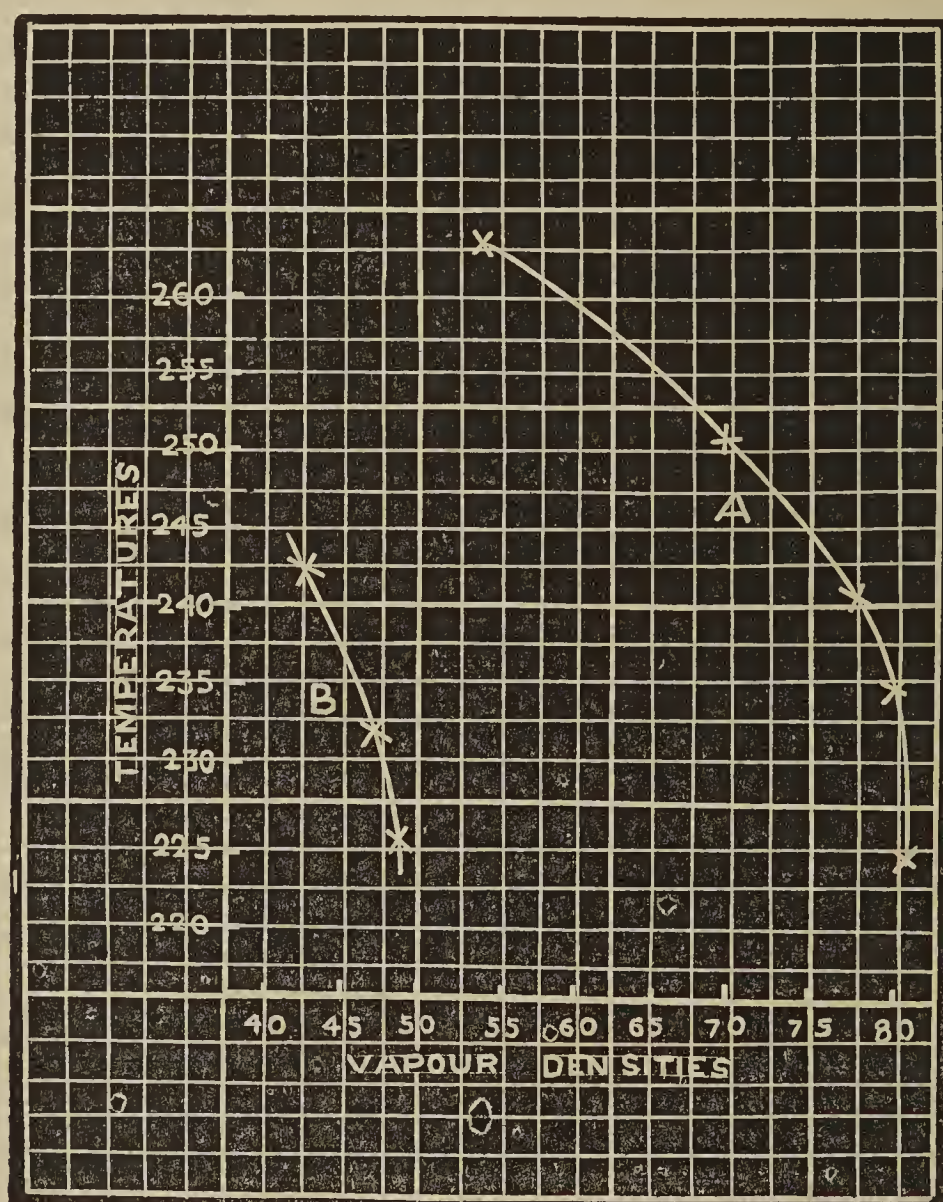
On tabulating these results for comparison, it is seen that the vapour density decreases as the temperature rises.

- (I.) $w = 0.0803$. Temperature $= 225^{\circ}$ to 226° .
 $v = 20.61$ c.c. $t = 11.5^{\circ}$. $P = 720.33$ m.m.
Vapour density $= 47.80$.
- (II.) $w = 0.0658$. Temperature $= 231^{\circ}$ to 232.5° .
 $v = 17.78$ c.c. $t = 13.6^{\circ}$. $P = 718.14$ m.m.
Vapour density $= 47.21$.
- (III.) $w = 0.0791$. Temperature $= 242^{\circ}$ to 243° .
 $v = 21.83$ c.c. $t = 16.3^{\circ}$. $P = 717.85$ m.m.
Vapour density $= 45.37$.

Tabulating again:—

Temperature.	Vapour density.
225.5°	47.80
231.7°	47.2
242.5°	45.4

Complete dissociation into $C_{10}H_{16}$ and HCl would require the density to be 43.17. That is already, at 225° , over 75 per cent of the hydrochloride has split up, and at 240° to 250° the dissociation is nearly complete. These results are represented by the curves on the diagram below, where



Temperature.	Vapour density.
224.0°	80.85
233.9	79.15
241.0	76.22
250.7	69.77
262.5	56.23

Theoretical vapour density calculated from the formula $C_{10}H_{17}Cl = 86.25$.

Hence at 224° about one-sixteenth of the compound is dissociated; at 262.5° about one-half.

Inactive camphene hydrochloride was prepared by passing dried hydrochloric acid gas through a saturated solution of inactive camphene in rectified spirit of wine, the vessel being kept cool.

The vapour density was determined in the same apparatus, at temperatures ranging from 225° to 243° ,

the ordinates represent the temperatures in degrees Centigrade, the abscissæ the vapour densities. Curve A relates to terpene hydrochloride, B to hydrochloride derived from camphene.

Hence camphene hydrochloride, which is more easily decomposed by water, is also less stable than terpene hydrochloride under the influence of heat.

Dr. Tilden has already shown (*Journ. Chem. Soc.*, 1884, p. 410) that, at a low red heat, the terpenes yield a considerable amount of isomeric terpine, and at the same time partly break up into isoprene and other products. But camphene at the same temperature appeared to be more stable, and gave no isoprene.

It was therefore a matter of interest, in connection with the present enquiry, to ascertain whether a similar difference was observable between these two hydrocarbons

at temperatures not far removed from the lowest temperature at which dissociation takes place.

The vapour density of turpentine has already been determined by Weyl (*Verhandlungen d. Physiol. Gesells. x. Berlin*, 1885-6, Nos. 1, 2) at the temperature of melting lead, and somewhat remarkably was found to agree very closely with the formula C_5H_8 , showing that at this temperature complete dissociation had taken place.

The following are the results of my own experiments. The vapour densities were again determined by Victor Meyer's method, but using a bath containing melted lead. Camphene, $C_{10}H_{16}$, = vapour density 68.

(I.) $w = 0.0472$.
 $v = 11.80$ c.c. $t = 19^\circ$. $P = 716.4$ m.m.
Vapour density = 49.5.

(II.) $w = 0.0673$.
 $v = 16.45$. $t = 20.5^\circ$. $P = 723.7$ m.m.
Vapour density = 51.5.
Mean = 50.5.

Turpentine, $C_{10}H_{16}$, = vapour density 68.

American turpentine, dried by calcium chloride and then re-distilled at 156° to 158° was used.

$w = 0.0372$.
 $v = 13.39$. $t = 20.3^\circ$. $P = 714.5$ m.m.
Vapour density = 34.62.

The formula C_5H_8 requires the vapour to have density = 34.

Weyl's experiments gave 39.2 and 38.6 for the vapour densities of turpentine.

Camphene, then, is much more stable than turpentine, for, whilst complete dissociation of the latter had taken place, only about 70 per cent of the former had broken up.

We have then, to account for the paradoxical result that the hydrochloride obtained from the stable hydrocarbon is less stable than that obtained from the unstable one. The following explanation was suggested to me by Dr. Tilden:—The stable hydrochloride obtained from terpene is probably a substitution compound of a hydrocarbon, $C_{10}H_{18}$. In it, then, the chlorine is probably directly combined with the carbon. The unstable compound, on the other hand, is most likely a molecular compound; in it the chlorine probably retains its hold upon the hydrogen atom of the acid at the same time that it is combined with one or more carbon atoms in the hydrocarbon.

My best thanks are due to Prof. Tilden and Dr. Nicol for much kind help and valuable suggestions.

ON THE

ATOMIC WEIGHT OF OXIDE OF GADOLINIUM.

By A. E. NORDENSKIÖLD.

As in previous communications, I mean by *oxide of gadolinium* the mixture of oxides which were first discovered in the gadolinite from Ytterby,—oxides characterised chemically by the fact of being precipitated from their solutions by ammonia, by oxalate of ammonia, and by neutral sulphate of potassium. It is now well known that this mixture, long thought to be a simple oxide, is composed of at least three oxides very close together chemically, although they have very different atomic weights. These oxides are the following:—

	Atomic Weight.*	1 grm. of Oxide gives of Neutral Sulphate.
Oxide of yttrium ..	227.2	2.056 grms.
„ erbium ..	380.0	1.632
„ ytterbium ..	392.0	1.612

Science not having yet found the means of separating elements which are so much alike, and at the same time so different in atomic weight, we are obliged, in order to be able to calculate the atomic composition of the minerals of which these oxides are a constituent part, to determine for each analysis the atomic weight of the mixed oxides.

I have recently made such a determination on the occasion of the analysis of a remarkable carbonated silicate of yttrium, erbium, and ytterbium (or of *gadolinium*), recently found at Hitteroe in Norway, and called *kainosite*. I found, on this occasion, that 1 grm. of oxide of gadolinium extracted from kainosite gave 1.922 grms. of neutral sulphate, corresponding to an atomic weight of the oxide of 260.2. On comparing this figure with the atomic weights got in the same way from oxide of gadolinium obtained from other minerals, I found to my great astonishment that the oxide of gadolinium, although it consists of a mixture of at least three oxides, whose atomic weights vary between 227 and 392 always has a constant atomic weight, whatever the mineral from which it was extracted.

The following table gives all the determination hitherto made on this subject:—

* Taking the atomic weight of oxygen as 16, and supposing these oxides to be formed according to the formula R_2O_3 .

	Acids, &c, entering into the constitution of the mineral.	Approximate percentage of Oxide of Gadolinium.	Grms. of Sulphate yielded by 1 grm. of Oxide of Gadolinium.	Atomic Weight of Oxide of Gadolinium.	
Gadolinite from Ytterby	SiO_2	50	1.923	260	A. E. Nordenskiöld.
Gadolinite from Karlberg, in Dalecarlia.. ..	SiO_2	34.6	1.908	264.2	G. Lindström.*
Kainosite from Hitteroe	SiO_2, CO_2	38	1.922	260.2	A. E. Nordenskiöld.†
Azzhenite from Ytterby	SiO_2, Ta_2O_5	33.2	1.910	263.8	N. Engström.‡
Xenotime from Hitteroe	P_2O_5	60	1.922	260.2	A. E. Nordenskiöld.
Fergusonite from Garta, near Arendal	Nb_2O_5	39	1.909	264	G. Lindström.
Fergusonite from Moss	Nb_2O_5	39	1.926	259.2	G. Lindström.
Cleveite from Garta	U_2O_4	10.1	1.909	264	G. Lindström and Cléve.
Fluocerite from Osterby, in Dalecarlia.. ..		2.5	1.919	261.2	A. E. Nordenskiöld.
Eudialite from Kangerdluarsuk, in Greenland	SiO_2	0.1	1.923	260	G. Lindström.
Mean.. ..			1.917	261.9	

* *Société Géologique Suédoise*, p. 218; 1874.

† *Ibid.*, 1886, p. 143.

‡ NILS ENGSTROM, *Undersökning af nagra mineral; som innehålla sallsynta jordarter*. Upsala, 1877.

|| *Société Géologique Suédoise*, p. 218; 1878.

The oxide of gadolinium employed by me or by M. Lindström for the determinations of the atomic weights given above, was produced in the following manner:—

Dissolve the mineral in muriatic or sulphuric acid. Remove the silicic, tantalic, niobic, &c., acids in the ordinary way. Precipitate the oxides of iron, aluminium, cerium, yttrium, &c., with ammonia.

Dissolve the ammoniacal precipitate in muriatic acid, and from the slightly acid solution precipitate the oxides of cerium, yttrium, &c., with oxalate of ammonium. Filter off the precipitate, heat it to redness, dissolve in sulphuric acid, and then separate the oxide of gadolinium from the oxides of cerium, lanthanum, &c., by precipitating the latter with a saturated solution of neutral sulphate of potassium. From the filtrate precipitate the oxide of gadolinium twice with ammonia to separate the potash, then with oxalate of ammonium. The oxide of gadolinium obtained in this manner by the ignition of the oxalate, contains neither oxide of cerium, lanthanum, didymium, nor potassium.

It is easy to determine the atomic weight by transforming a weighed quantity of the oxide into sulphate by digesting it with hydrated sulphuric acid and evaporating off the excess of water and sulphuric acid until the commencement of a dull red heat. The heated sulphate dissolves easily in cold water. The solution is seldom quite clear; however, the residue is always insignificant if care is taken. If the crude mineral contains phosphoric acid, examine specially if the oxide is free from this substance; it is easily separated by repeated precipitations with oxalate of ammonium.

The minerals mentioned in the above table come from seven localities far removed from each other*; their bases are united with totally different acids; the determinations of the atomic weights have been made by different people, whose mode of operating naturally has not been quite the same. The accord seen to exist between the atomic weights of the mixture which I have called oxide of gadolinium, extracted from ten different minerals is very remarkable. It is quite as close as the accord between the determinations by different chemists of the atomic weights of most of the better known elements. The greatest divergence from mean is here 1 per cent, while, for example, the atomic weight of aluminium has been altered of late years about 1.5 per cent, that of oxygen 0.25 per cent, that of nickel 1 per cent, and that of magnesium 5 per cent. The variations in these cases are within the limits of observation, while in the case of oxide of gadolinium they are due to the difficulty of eliminating entirely the excess of acid by heat, without forming traces of basic salt, and of completely separating by means of sulphate of potassium the oxides of cerium, &c., from oxide of gadolinium. I am therefore perfectly authorised in saying:—

That oxide of gadolinium, although it is not the oxide of a simple body, but a mixture of three isomorphous oxides, even when it is derived from totally different minerals found in localities far apart from one another, possesses a constant atomic weight.

Still, we have here to do with an isomorphous mixture and not with a true chemical compound. We are, therefore, in presence of a fact altogether new in chemistry and mineralogy. It is true we have thousands of instances of isomorphous oxides reciprocally replacing each other, as, for example, oxide of iron and alumina, or lime, magnesia, protoxide of iron and of manganese; but this is the first time we are confronted with the fact that three isomorphous substances, of a kind that chemists as yet are forced to regard as elements, occur in nature not only always together, but in the same proportions. It seems that chemists here find themselves face to face with a problem

analogous to that presented to astronomers in the origin of the minor planets.—*Comptes Rendus*, vol. 103, p. 795, Nov. 2, 1886.

NOTE ON PROF. L. SMITH'S PLAN FOR ESTIMATING THE ALKALIES IN SILICATES.

By PHILIP HOLLAND,
Public Analyst for Southport.

HAVING had occasion, at times, to estimate the alkalies in silicates, I adopted the plan of fusing them with calcic oxide and chloride, strictly following the instructions of Lawrence Smith. This method is probably sufficiently familiar to most analysts, and need not be set down here.

Those, however, who may not be conversant with the scheme in detail, I would refer to "Select Methods in Chemical Analysis," Ed. 2, p. 28, *et seq.*

The few experiments that form the matter of this note were recently made just to test the process in one or two particulars which I had not done hitherto.

On turning to the English translation of Fresenius, Ed. 7, vol. i., p. 353, will be found the amounts of CaCO_3 , recommended by Smith and by Deville, with which to fuse one part of a silicate. The French chemist, as all are aware, has, antecedently to Smith, used lime for opening up silicates, but, according to the latter, for a somewhat different purpose to himself, and this may account for the wide difference in the quantities quoted by Fresenius.

Smith remarks, after describing his own process at length "Its constant accuracy still lacked some little to render it perfect as usually an amount of alkali remained behind, amounting to $\frac{1}{10}$ to 1 per cent of the mineral used,—certainly a small quantity, but still too much to be omitted in an accurate analysis" (Smith recovers this by again fusing the residue with extra NH_4Cl , and adds it to the principal amount). The statement that one per cent of alkali remained usually behind in the residue caused me surprise, and from experiments lately made on felspathic rocks I find that all the alkali is obtainable by a single fusion, in their case at any rate. I said, above, that I strictly followed Smith's instructions. This was so in all important points, as for instance in the preparation of the precipitated CaCO_3 (powdered Iceland spar not answering so well), the use of his form of crucible, the manner of heating it, and duration of the fusion. I should state that my reagents contained a little alkaline salts, deriving them, no doubt, from the bottles in which their solutions are preserved.

This trace, if I may use the term to indicate 2.8 m.grms., was first estimated in the total amount of reagents used, which was the same for all the later experiments, and was allowed for.

The blank trials, of which I am now speaking, were made on a mixture of 6 grms. of CaCO_3 with 0.75 of NH_4Cl , this being the one that Smith uses to decompose 1 grm. of a silicate. The crucible containing it was heated gently at first and then strongly for the time specified, viz., forty minutes. When cold the fusion was removed and extracted in a platinum basin, and the filtrate treated as usual for separating the alkaline chlorides.

The following are the weights of the chlorides so obtained, in which KCl was easily detected by PtCl_4 . The major portion is NaCl:—

M.grms.
3.2
2.4
2.8

A point that seemed desirable next to establish was the loss, if any, occurring when a known weight of mixed chlorides is fused along with the CaCO_3 and CaCl_2 . It

* Ytterby is situated on the western side of Sweden; Karlberg and Osterby in central Sweden; Moss is to the east of Christiania (Norway); Garta and Hitteroe are in the southern part of Norway; Kangerdluarsuk is in Greenland.

Name of Silicate.	Mixed Chlorides.	K ₂ PtCl ₆ .	K ₂ O.	Na ₂ O.	Mixed Chlorides obtained on re-fusion. M.grms.
Basaltic rock, "Cader Idris," N. Wales	13.05	21.34	4.19	3.46	4.0
" " "Dunmail Rise," Westmoreland..	11.18	10.10	1.95	4.29	3.2
Leucitic rock, Rieden, Germany	24.72	42.33	8.17	6.25	3.4
Red spongy lava, Pompeii	14.34	31.44	6.07	2.51	3.8
Syenite, "Yr Eifl," N. Wales	16.36	21.82	4.21	5.14	2.9
" Nevin, "	16.17	17.99	3.473	5.662	3.6
" " " "	16.24	17.98	3.471	5.700	4.0
" " " "	16.30	18.00	3.475	5.750	3.0
" Llanbedrog "	15.90	27.02	5.21	4.05	3.6
Vitrified ash from a bush fire, Natal	9.44	27.48	5.30	0.53	

was, perhaps, too much to expect that slight loss should not occur. It is, however, hardly of any account, as will be seen presently.

The mixed chlorides, consisting of pure KCl and NaCl fused together and powdered, had the following composition:—

	1.	2.	Mean.
KCl.. ..	54.072	54.117	54.094
NaCl	45.928	45.883	45.905

In one experiment I took of this 0.2362 grm., and in a second 0.3173, and in each instance fused with the specified weights of CaCO₃ and NH₄Cl for forty minutes. The recovered salts, *after deducting* 2.8 m.grms., weighed respectively 0.2345 and 0.3152 grm. It is, perhaps, scarcely necessary to say that when removing ammoniacal salts by ignition, the loss of alkaline chlorides may extend to several m.grms. if the operation be hastily conducted, or the dish too strongly heated by a naked flame.

The recovered salts in the first experiment weighing actually 0.2373 grms., were dissolved in water and the potassium chloride estimated by PtCl₄.

Found, 0.4146 K₂PtCl₆ = 0.1266 KCl, giving as the composition—

KCl	53.35
NaCl	46.64

Of the silicates mentioned in the above table 1 grm. was taken in exceedingly fine powder and thoroughly mixed with 6 grms. of CaCO₃ and 0.75 grm. of NH₄Cl. The fusion, after first heating the mixture gently to form CaCl₂, which, according to Smith, plays so important a part in his process, lasted forty minutes. †

Special care was taken that the resulting chlorides of the alkalis were pure before final weighing and separation by PtCl₄. The potassium salt was collected in the Gooch crucible and treated with alcohol to remove PtCl₄ and Na₂PtCl₆. A slight washing was also given with a solution of K₂PtCl₆ in NH₄Cl to remove any still remaining Na₂PtCl₆, and a final one with alcohol.

The conclusion to which these figures point is that fusion with lime does practically extract all the alkali at one operation, that concordant results are obtainable, and that by use of a crucible of the form recommended by Prof. Smith, the loss of salts by volatilisation is reduced to a minimum.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 233.)

It occurred to me that we might make use of the reaction which takes place between the alkaline fluorides and fluoride of aluminium, in order to show, after the elimination of silicon as a fluoride, the presence of aluminium,—an operation which is by no means easy if we use the ordinary methods, which are not at all adapted to the use of

the microscope. From this point of view it seemed to me to be necessary to study the behaviour of the other tri-valent metals.

Now I found that the fluo-aluminate of sodium is isomorphous with the combinations, of sodic fluoride, on the one hand, and the ferric, manganic, chromic, and uranic fluorides, on the other. In the reaction we can substitute the chloride for the fluoride of sodium; if we use an excess of sea-salt we observe, instead of little hexagonal plates, a figure imitating a flower with six leaves, which strongly reminds us of snow crystals. Furthermore, the resemblance of the crystalline forms goes much further in the case of the fluo-salts.

The before-mentioned double salts are analogous, as to their form, with the corresponding fluostannates, fluotungstates, fluomolybdates, fluotantalates, and fluoniobates; the fluoborates, fluotitanates, and the fluozirconates, on the contrary, are sensibly different.

The sodic fluoborate resembles the fluosilicate of the same metal; the same is true of the fluotitanate, but the crystals of this latter salts are not very definitely formed. It separates slowly in the form of little rounded masses, which, after the lapse of about ten minutes, gradually take the form of a hexagon. The sodic fluozirconate appears much sooner; its crystals are four-sided pyramids.

The potassic fluoborate has the same form as the corresponding fluotitanate; both crystallise under the forms of rhombs, often having the angles truncated. The rhombic crystals of the titanate are very apt to form raphides, because of the extraordinary development of a pair of truncating planes. The fluozirconate behaves altogether differently; it appears to be only slightly soluble; it can only be obtained in the form of very thin grains: the same phenomenon was observed with the fluozirconate of calcium, whilst the fluotitanate of this metal is, on the contrary, very soluble in water.

I have dwelt at some length on these reactions, because they seemed to be able to furnish me with a means of deciding whether certain reddish yellow crystals found in gabbro, and eklogite, were rutile or zircon.

M. Marignac* has attributed to some of the fluo-salts described a different crystalline form to which I did. I therefore repeated my experiments, but always with the same results.

I think I may attribute this discordance to a difference in the development of the facets.

I have not gone more fully into this subject for the reason that the study of the fluo-salts had only a secondary interest for me, and would only keep me from the principal aim I had in view.

After being convinced that M. Boricky's method does not enable us to determine the presence of calcium and magnesium with the accuracy wished for, and that it might lead us to confound silicon with aluminium, and this latter element with boron and iron, and to a certain extent with manganese and chromium, I found it necessary to abandon it, and to try and devise another, which, although less simple and elegant, enables us to obtain

* *Ann. de Chim. et de Phys.*, vol. lx., p. 301.

Results of greater certainty, and more decisive, in a shorter time and with greater ease.

4. *New Micro-chemical Method.*

A complete system of micro-chemical methods, in the study of petrography, ought to furnish means sufficient—

1st. For the qualitative analysis of the small fragments of minerals which frequently occur. The minimum weight of these fragments may be taken at 0.1 m.grm., which corresponds to a diameter of about 0.3 m.m.

2nd. For the qualitative search for the integral particles, at different points on the polished surface of a mineral.

3rd. For the separation of the fragments of the more common minerals, so as to complete the qualitative by a quantitative analysis.

The reactions comprised under the first of these requirements ought further to satisfy the following conditions:—

a. Filtration must be entirely dispensed with, thus preventing, as much as possible, waste of time and contamination of the substance under examination by foreign matter.

b. Chemical compounds must be formed which are easily recognisable, either by their crystalline form under the microscope or by the formation of intensely coloured precipitates.

c. The time required to form distinct crystals, during a slow evaporation, must be as short as possible; two hours at the most should suffice for these operations.

d. All the phenomena to be observed must be of such clearness and simplicity that anyone, with very little practice, can make use of them with success.

Thus it is necessary to endeavour to make use of reagents having a high molecular weight; it would even be advantageous to give the preference to those reagents which form double salts, rather than to those which only lead to the formation of simple salts of equal solubility; and further, it will be easily understood that the formation of salts containing water of crystallisation will always have an advantage over that of anhydrous salts.

5. *Preparation of the Mineral for Examination.*

1. When we have large quantities of the mineral available, or several samples and specimens from the same neighbourhood, it is often advantageous to detach small splinters by means of a hammer, and then pick out from the fragments all the particles of one particular mineral. I generally adopt this method when the crystals have a linear dimension of 1.5 m.m. We must then make sure, by examination with the glass, that we have to deal with particles of identical structure, colour, and brilliancy, and when necessary we must free the mineral from traces of iron by treatment with aqua regia.

2. Micro-crystalline rocks must be crushed in an agate mortar, or, when one is not available, on a small anvil, while wrapped up in paper. After having got rid of the dust by sifting or blowing gently on the powdered mineral, we must try and pick out, by the help of a glass or a low power microscope, either with a needle or a small pair of tweezers, all the homogeneous particles we can find of the mineral under examination. By moistening the needle with glycerin it is more easy to remove the small particle, and by then plunging the point of the needle into water the mineral will drop off.

3. In cases when we cannot easily distinguish the integral parts of the rock in the accompanying substance, we make use of a plate sufficiently thin that it has enough transparency to be used with a microscope multiplying 100 times. The plate must be slightly polished, to effect which we must stop adding emery, and, on the contrary, keep adding water, while rubbing the mineral on the plate with a gentle circular movement, until there is nothing left between the mineral and the plate of iron on which it is being ground. In certain cases we can give the plates

the transparency necessary for use with a lower power microscope, by moistening them with glycerin or olive-oil.

In microscopic researches it is necessary that the Canada balsam which is between the mineral substance and the slide should have a certain softness; it may sometimes be necessary to bring this about by gently heating.

We can now detach under the microscope (making use of an object-glass of low, and an eye-glass of high, power) small particles of the mineral by the aid of a small thin blade, or a large needle ground flat at the end so as to form a knife, so that the cracks will not spread far from the field of vision. We must operate by commencing at the edge and gradually advancing to the centre, and then, by heating rather strongly and scratching on the surface, we are able to remove the particles of foreign matter which are detached. We can in the same manner remove the segment of the mineral required for the experiment, and by heating it strongly drive off all organic matter. Finally, the little particles of adhering matter can be got rid of in the manner described above (No. 2).

In order to facilitate the action of the chemical reagents the mineral must be reduced to a very fine powder, and to prevent loss the lumps must be covered with paper before breaking them up in a steel mortar. The paper can be removed with the aid of a steel or horn knife, but glass, porcelain, or bone must never be used. The steel blade can also be used to collect the powder adhering either to the pestle or the mortar.

(To be continued.)

THE HISTORY OF CALIFORNIAN BORAX.

By ARTHUR ROBOTOM

SIR EDWARD BULWER LYTTON, in the "Last Days of Pompeii," bears testimony to the value set upon borax in the days of the Roman republic. "Borax," says Sir Edward, "was largely used by Nero and his slaves near 2000 years ago, and Pansa deeply regretted that he was not rich enough to buy borax to cover the arena after the death of the combatants at the time of the fight between Lydon and Tetraides." Many a time since my visit to the Californian borax districts has this passage sprung into my mind, and often I have thought what a pity it was that Olanthus, Glaucus, Caligula, and the gladiators did not know of the existence of the great borax lake in Slate Range Mountains, California.

My visit to this lake was one of the most interesting journeys I think I ever made in my life, and the accident of my making this journey arose in the following manner. In the year 1874 I visited the borax deposits in Nevada, and was on my way to San Francisco, when during the journey I was interviewed by a reporter of a Winnemucca newspaper, who, without my knowledge, sent on to San Francisco the following particulars concerning my visit in his paper, and which were duly reproduced before my arrival in the "Californian Alta," of San Francisco:—"Mr. Arthur Robottom, of Birmingham, England, paid our town a visit a few days ago, on a prospecting tour, to discover if any borate of soda or borate of lime exists in this section. He was much struck with the number of hot springs that are to be found all through the Humboldt Valley. The borate of soda and borate of lime are known to exist at Hot Springs station on the Central Pacific Railroad, also at Columbus and other parts of this State; and no doubt if the hot springs of Humboldt Valley should prove to give off vapours that produce boracic acid, or that borate of soda is to be found in the alkaline beds which exist all over the district, a new and profitable trade will spring up. The article of borax has been well known all over the civilised world; still but

few people know anything of its origin. In 1818 Count Lardarel discovered how to prepare boracic acid from the Lagoons of Tuscany, and made a princely fortune by it. This boracic acid was shipped to England and France and converted into refined borax by boiling in large pans, and crystallising in vats. Tincal was the artical used in making borax before boracic acid was discovered. This article is found on the dreary plains of Thibet, in Asia, and sent on sheeps' backs across the Himalaya Mountains to Calcutta, and thence to England. About 20 years ago borate of lime was discovered in Chili, and found its way to England, Mr. Robottom being one of the first to introduce it into that country. Mr. Robottom will also visit the Hot Springs, Wadsworth, Columbus, and San Francisco." The result of this having appeared was that the morning after my arrival in San Francisco my hotel was fairly besieged with persons who were anxious to interview me in my capacity as a borax expert. After many interviews with individuals who professed to hold land said to be rich in borax, I decided to visit and inspect the great Slate Range district, and after making all my arrangements I left San Francisco, proceeding southwards by steamer down the Pacific coast, and after a pleasant journey arrived at Los Angeles or City of Angels, an old Mexican town. Los Angeles is now, however, peopled principally with Americans, who drive a considerable trade with the teamsters who visit the interior. At this time the Southern Pacific Railway was not made, and this section of the country could be traversed only by the aid of mule teams; the Slate Range lay about 240 miles inland, and the whole country was infested with a band of ruffianly bandits and robbers, composed of the very refuse of society from all parts of California and Nevada. Under these circumstances I soon discovered that my only chance of travelling with any safety was to assume the rôle of what is known in this part of the world as a "busted" miner, "busted" being a convertible term for ruined, and derived probably from "bursting," or broken up. I was also informed that on some parts of the journey, hay was worth £50 per ton, and water two shillings per bucket, and that it would be better for me to walk, and much safer. Adapting myself to the circumstances I started in my disguise and travelled with a mule team over a very rough country at the rate of from 12 to 14 miles per day, and arrived at length, without any remarkable adventure, at the shanty kept by Jim Bridger, some 42 miles from the Slate Range, and which is situated on the main road to Cerre Gorda, a wild looking spot, without any other road, the country being covered with the oleaginous plant known as greasewood, and the only animal life being represented by the dismal owl and the deadly rattlesnake! Not a very pleasant prospect, I thought, but I afterwards found when sleeping out in this part of the country that by surrounding myself with the ashes of a greasewood fire or a horsehair rope, that as far as the rattlesnakes were concerned there was no danger, as these reptiles, strangely enough, will never cross the ashes of a greasewood plant, or a rope made of horsehair. While as to the owl his existence was naturally a pure matter of indifference to me, so far as my comfort was concerned.

Rather a curious incident occurred to me while staying at Jim Bridges': a pioneer and prospector had come from the mountains to get a few supplies from the store, when he saw me sitting on a bench outside, and after a few words had passed, he remarked, "Why you are from the Old Country, and pretty green too! whatever brings you into a country like this? You are no miner! Have you been writing somebody's name on a bit of paper, or done some act as you're afraid of the Sheriff; or are you on the wrong side with the other sex?" My reply was that I was all right on these points, and had come out here prospecting for borax. He at once begged me to have nothing to do with it. He said, "There is plenty of it, but no one knows what it's good for." He had been down to Death Valley, and to the foot of the hills of the Slate Range, through Owen's Valley, and to Mono Lake, and

he gave me much information about this "howling wilderness."

After a short stay at Jim Bridger's shanty I again proceeded, steering for the Foot Hills, some 22 miles from the shanty, then onward through a great canon, or divide, partly covered with salt, on emerging from which I found myself on the border of the most important borax lake yet discovered in the world. I was met by John and Dennis Searle, two men belonging to the Californian discovery army that sprang into existence in the year of 1849, and whose members are known by the name of "Forty Niner's." These men, masters of almost every kind of handicraft, had made their way to this great lake with a view to exploration. Consequently, though I can claim to be the first Englishman who visited the borax lake, the honour of its discovery does not rest with me. I stayed some time in the hut of these men, and together we examined the ground. I very soon discovered natural borax of the finest quality in a pure state, and though Messrs. John and Dennis Searle had begun prior to my arrival to develop the ground, the first shipment was made by me to England. The borax I found was crystallised borax, in the same form as the regular borax of commerce, and is the only known deposit of natural borax yet discovered in the world. In the centre of the lake is a bed of salt about five miles long; on the outside of this salt is a deposit of carbonate of soda, and some thousands of acres of land covered with crude borax, from three inches to two feet thick. The crude borax is collected and put into cowhide baskets, carried to a large boiling-pan, and boiled for 36 hours; the solution is then run into vats and the crystals form on the sides of the vats. After drying it is put into bags, about 70 lbs. in each bag, and sent to San Francisco, a distance of about 420 miles, and conveyed at that time by mule teams. Before leaving California I arranged to buy 1280 acres of this borax land; I returned to England as quickly as possible, made arrangements to go out again, formed a small company who put up works, and I anticipated making about a million by it, and before long we began to ship large supplies of borax to Liverpool, London, and New York. The price, however, suddenly came down to £26 per ton, the lowest price it had ever been sold for, while the carriage alone from the lake to San Francisco at this time was about £16 per ton of 2000 lbs. This was a paralysing condition of affairs that quite stunned me. I had made a very large contract for some hundreds of tons to a large firm in England, but before the arrival of the ship with the first parcel the firm failed, and I found myself, to my horror, with some hundreds of tons of borax left on my hands that I could not get rid of, the bankers and financial houses holding the documents all pressing for sales to be made! My golden dream of making a million faded away, and left me meditating the bitter realities of impending ruin! (I yet anticipated that this property will at some future period be worth £1000 per acre. Experience has proved that the crude borate of soda on the surface of the land reproduces itself every three years.). As soon, however, as I had somewhat recovered from my shock I began to realise that I must do my utmost to find a market for the borax. I was driven to every move that a man could suggest to try and begin to get clear of the stock. I knew that if the public could only be made to understand the true merits of the article, and would begin to try it, all would come right for myself and friends. Consequently I set to work, and began to have the ground borax packed in penny packets. Here again I met with disappointment, for I soon found out that the public are very slow in taking to a new article, and I could not induce the retail shopkeepers to sell it. I offered it to the druggists, they all replied "you want us to sell far too much for a penny, we want eightpence for what you want a penny for; 25 per cent profit won't pay us." I then tried the grocers; they were satisfied with 25 per cent profit, or less, but their reply was as characteristically disheartening. "It's all right," they said, "but borax is some kind of medicine, not a

grocer's article, we can have nothing to do with it—it's too much trouble to tell the customers its merits." The whole business began to look very dark and gloomy; almost in despair I took a stand at the first dairy show in the Agricultural Hall, and met with marvellous success. I then tried many of the laundries in and about the suburbs of London, and I also tried many of the hospitals and other public places with more or less success.

A lady, universally known from her philanthropy, sent her almoner to see me about it, and a specimen was sent by her desire to one of the first scientists of the day; but the true merits of borax were not then known even to the wisest of the wise. My belief in the borax, however, has never deserted me. I made many experiments and collected much information as to its uses, and the consumption during the last few years has very considerably increased; but this has only occurred since I parted with my interest to the Patent Borax Company of Birmingham, who have naturally been enabled to bring the product more forcibly to the front as one of the most useful and important products yet discovered in the world. I still feel a very keen interest in the future of this product, though I have no pecuniary end to serve in saying so; but the multiplicity of its uses is truly marvellous, and the following information cannot, in my humble opinion, have too extended a circulation. For the laundry there is a very great deal of labour saved by using borax, as this product "softens" the dirt, and the latter may almost be said to float out of the linen, saving at once the destructive friction, and the time and materials. For the household its uses are legion; beds, &c., washed with a strong solution of borax in the spring, prevents insect life from forming; dusting the floors with dry borax destroys the larvæ of the moth, and keeps the carpets entirely free from insect life. For cleaning marble, plate, jewellery, decanters, plates; for improving the flavour of boiled vegetables, tea, &c., and preserving eggs, fish, butter, and milk, borax, in one or other preparations, is simply invaluable. It is the best tooth-wash known; will clean brushes, sponges, &c., from dirt. Medicinally the value of borax is not as fully known as it should be. I hold letters from eminent medical men who have corresponded with me upon its value, and who esteem it highly. The *Lancet*, of May 20th, 1876, contained a laudatory article on it as a valuable antiseptic "which does not irritate and inflame." I have cured thousands of persons suffering from sore throat, by giving them a small piece of borax to suck (I always carry a bit in my pocket wherever I go); and for dissolving the phlegm and clearing the throats of speakers, my own experience proves to me that it is the only reliable remedy.

Since the first publication of the above, extensive progress has been made in the development of the uses of borax by the general public; and from letters, the thanks and encouragement I am receiving from many friends and strangers satisfy me that I have given information which well repays me for all the trouble, losses, and the inconveniences I have been put to in trying to make this wonderful production better known.

Touching the labour uses of borax, it is mainly used in glazing all descriptions of porcelain, china-ware, pottery, &c. Blacksmiths use it for welding iron and steel. It is used for welding the seams of copper and iron tubes; in the manufacture of hats, jewellery, artificial diamonds, and the plates for affixing artificial teeth. The finest marble cement is made from borax. Farmers, graziers, &c., use it for washing cattle; and provision merchants for arresting or preventing decomposition in their hams, &c. The foregoing will, I trust, awaken people to an interest in this most valuable product of the earth.

Native Borax.—Analysis:—

Sodium baborate—pure	99.75
„ chloride—trace only	0.25
	100.00

The following are the rates of wages paid for labour in this section:—

	£	s.	d.	
Blacksmiths	1	0	10	per day.
„ helpers	0	12	6	„
Engineers	0	16	8	„
Teamsters	0	13	6	„
Coopers	0	13	6	„
Boilermen	0	10	6	„
Watchmen	0	10	6	„
Labourers, principally Chinamen	0	5	3	„

The Southern Pacific Railway Station is only about 72 miles from the Lake, where the borax is carried by 20 mule teams, but in about three years or less a railway will run within four miles of this desolate country, when these wonderful natural deposits will be more carefully examined by scientific men.

Before concluding this article, I may here state the borax lake is not a very enviable place to live in. On my first visit, Jim Bridger's shanty (42 miles from the lake) was the nearest place from which we could obtain our coffee, sugar, or canned fruits, &c., and post our letters. We had no drinkable water within 17 miles. Always a clear blue sky (a little London fog would have been a great treat). Not a tree visible; no vegetable, only the oleaginous greasewood plant. No animal life, no Indians, no clouds, no rain; and last, but not least, a total absence of the fair sex. The freight alone to build our works cost 2½d. per lb. from San Francisco.

107, Dunster House, Mincing Lane, London, E.C.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 236.)

ON the conclusion of the president's address it was moved and carried that the order of business adopted for the previous meeting be continued for the present as follows:—

(1) Reports of committees:—(a) on Phosphoric Acid; (b) on Potash; (c) on Nitrogen—the reports to be received and discussed in this order.

(2) Determining methods to be used during the next year, in the same order.

(3) Election of officers.

(4) Miscellaneous business.

In accordance therewith the report of the Committee on Phosphoric Acid was presented by the Chairman, Dr. H. C. White, of Georgia, as follows:—

Report of the Committee on Phosphoric Acid.

The Committee on Phosphoric Acid respectfully submits the following report:—

Adopting the plan followed by the Committee last year, the report presents (1) brief notices of new analytical methods for determining P_2O_5 proposed during the year; (2) results of co-operative work done by the Committee and members of the Association; (3) recommendations for the next year.

The publication since our last meeting of the second edition (1886) of Crookes's "Select Methods in Chemical Analysis" has presented in convenient form outlines of nearly all methods for determining P_2O_5 worthy of note that have been suggested to the beginning of the current year. In addition we note as follows:—H. Joulie (*Ann. Agronom.*, ix., 97—129; Abstract CHEMICAL NEWS, lii, 85) re-publishes his "citro-uranic" method for estimating P_2O_5 in manures by dissolving in HCl, precipitating as magnesium-ammonium phosphate in presence of excess of citric acid, dissolving the precipitate in dilute HNO_3 .

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C., August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

with addition of sodic acetate, and titrating with uranic nitrate. He compares unfavourably the ordinary nitromolybdate method. The essential points in the process, with critical remarks, are given in Crookes's "Select Methods," Second Edition, 504-5 and in more detail in CHEMICAL NEWS Abstract (lii., 85). J. M. H. Munro adds to the Abstract in CHEMICAL NEWS some examples of tests of Joulie's method, indorsing it if carried out exactly as recommended.

M. Meinecke (*Repertorium Anal. Chem.*, v., 153; CHEM. NEWS, liii., 53) proposes to determine P_2O_5 by direct weighing of the precipitate of ammonium phosphomolybdate after heating for fifteen minutes at a temperature of 400° to 500° C. The composition of the black compound thus obtained is said to be constant, containing 4.018 per cent P_2O_5 . Certain precautions in precipitating with molybdate solution, washing, and drying, are pointed out as necessary.

Tests of this method, made in the laboratory of the Chairman of the Committee, have given unsatisfactory results.

E. Aubin (*Comptes Rendus*, c. 1595-6; *Journ. Chem. Soc.* Abstract, xlviii., 1093) avoids the precipitation of silica, lime, magnesia, fluorine, &c., and determines P_2O_5 by immediate precipitation with magnesia mixture as follows:—The sample is dissolved in boiling HCl with addition of a saturated solution of sodic acetate in acetic acid, solid ammoniac oxalate being added during the boiling. The precipitate is allowed to settle, filtered, and well washed. Excess of ammonia and solution of ammoniac citrate is added to the filtrate, which is then precipitated in the usual manner with magnesia mixture.

The Committee calls special attention to the very interesting and valuable paper of Dr. Paul Wagner (*Chemiker Zeitung*, x., 13; translated in CHEMICAL NEWS, liii., 133—136). Dr. Wagner has attempted by crop experiments to establish the relative manurial value of the "water insoluble" P_2O_5 in different classes of phosphates, compared with that of the "water soluble," and to devise an analytical method for the determination of what he calls "soluble" P_2O_5 (corresponding to what we designate "available") in either a superphosphate or a phosphate containing no "water soluble" P_2O_5 which method shall yield results corresponding to the proportionate manurial values.

The method proposed is as follows:—5 grms. of the sample are rubbed up with some dilute citrate solution poured into a half-litre flask, made up to the mark with dilute citrate solution, allowed to stand about 18 hours at the temperature of the room (13° to 18° C.), with frequent shaking, and then filtered. Fifty c.c. of the filtrate are taken and the P_2O_5 determined in the usual manner by molybdate and magnesia mixture. The citrate solutions are made as follows:—

(1) Concentrated citrate solution. 150 grms. of citric acid are placed in a litre flask, dissolved in water and neutralised with ammonia. To the neutralised solution 10 grms. of citric acid are added, and the solution made up to the mark with water.

(2) Dilute citrate solution. 1 volume of concentrated citrate solution is mixed with 4 volumes of water.

The other reagents are essentially the same as those now used by this Association.

At a meeting of the manure manufacturers of South Germany and representatives of the experiment stations of Bonn, Darmstadt, Marburg, Spier, and Wiesbaden, held at Mayence November 30, 1885, this method for the analysis of all superphosphates was unanimously agreed upon to be used from January, 1886, and the term "soluble" was adopted to designate the P_2O_5 extracted by the process indicated.

In view of the possible importance of the method suggested, should it be generally adopted by continental chemists, the Chairman of the Committee has made a few experiments to test the results given.

The samples of superphosphates A, B, and C, distri-

buted to members of the Association, as hereinafter described, were used in the experiments.

(1.) Five grms. of the superphosphate were treated directly by Wagner's method, with the following results:—

	A.	B.	C.
"Soluble" (Wagner) ..	8.35 8.37 8.40	12.10 12.15 12.14	9.95 10.01 9.96
Mean.. ..	8.37	12.13	9.97

(2.) Five grms. were first exhausted with pure water⁶ as in our ordinary method of determining "water-soluble," and the residue was then treated by Wagner's method.

	A.	B.	C.
Water soluble	7.40	11.50	9.15
Obtained from residue	2.25 2.20	1.52 1.50	1.75 1.68
Mean	2.23	1.51	1.71
"Soluble" (Wagner)	9.63	13.01	10.86

It is very evident that Wagner's method gives much lower percentages of what we are accustomed to call "available" P_2O_5 than the method now in use by us. The introduction of this method into our work would clearly be attended with many embarrassments; and yet, if Dr. Wagner's crop experiments and his conclusions are to be relied on, it is a question if his analytical method is not a proper one to employ in the official work of experiment stations and State officers. It will be remembered that considerations of a similar character led to the adoption by this Association of the temperature of 65° C. for digestion of the citrate solution in determination of "insoluble" P_2O_5 .

II. Owing to absorbing engagements of the Chairman the Committee was somewhat tardy this year in the distribution of samples for co-operative work. Finally, on June 12, three samples of superphosphates were sent to each member of the Association and to others, marked as follows:—

A.—Acid Phosphate, South Carolina.

B.—Acid Phosphate, Navassa.

C.—Acid Phosphate, South Carolina and Navassa mixed.

These materials had been specially furnished by courteous manufacturers, and were carefully sifted and mixed so as to secure uniformity. In the circular letter accompanying the samples request was made that the determinations be made within the week beginning Monday, June 28.

Returns have been received from eleven laboratories, covering the work of fifteen analysts. The results in full are here given:—

Results of Phosphoric Acid Determinations.

Analyst.					In-		
Sample A.		Moisture.	Soluble.	Reverted.	soluble.	Available.	Total.
A	..	7.15	7.16	4.29	7.61	11.45	19.06
B	..	7.02	6.63	5.00	7.31	11.63	18.94
C	..	7.05	7.01	5.33	7.04	12.34	19.38
D	..	—	6.98	5.09	7.48	11.07	18.55
E	..	6.27	7.00	5.05	7.01	12.06	19.06
F	..	6.27	6.99	5.01	7.04	12.00	19.03
G	..	7.14	7.01	3.97	7.71	10.98	18.69
H	..	—	7.15	3.77	7.77	10.92	18.69
I	..	6.88	7.05	4.69	7.35	11.74	19.09
K	..	7.22	7.04	5.24	6.75	12.28	19.03
L	..	7.17	7.46	5.06	6.42	12.52	18.94
M	..	8.70	7.12	3.76	8.04	10.88	18.92
N	..	—	6.90	4.29	7.87	11.19	19.06
O	..	7.25	7.40	5.16	6.40	12.56	18.96
P	..	7.20	7.32	5.09	6.45	12.41	18.86

Analyst.	Sample B.	Moisture.	Soluble.	Reverted.	In-soluble.	Available.	Total.
A	..	9.65	11.13	4.08	3.85	15.21	19.06
B	..	10.06	10.11	5.06	3.41	15.17	18.58
C	..	10.03	10.72	4.82	3.58	15.54	19.12
D	..	—	10.03	4.39	3.87	14.42	18.29
E	..	9.17	10.51	—	—	—	18.47
F	..	9.17	10.54	4.26	3.58	14.80	18.38
G	..	10.14	11.30	3.46	3.56	14.75	18.31
H	..	—	11.23	3.23	3.84	14.45	18.29
I	..	10.16	11.05	4.29	3.49	15.34	18.83
K	..	10.15	11.39	3.51	3.80	14.90	18.70
L	..	10.11	11.55	3.88	3.00	15.43	18.43
M	..	11.87	11.24	3.26	3.82	14.50	18.32
N	..	—	10.54	4.12	3.91	14.66	18.56
O	..	10.20	11.50	3.85	3.10	15.35	18.45
P	..	10.20	11.58	3.76	3.17	15.34	18.51

Sample C.

A	..	10.35	9.08	4.15	5.13	13.23	18.30
B	..	10.30	8.67	4.27	4.83	12.94	17.77
C	..	10.40	8.99	4.62	4.72	13.61	18.33
D	..	—	8.68	3.50	5.40	12.18	17.58
E	..	9.62	8.70	4.17	4.91	12.87	17.88
F	..	9.62	8.75	4.23	4.68	12.98	17.66
G	..	10.15	8.84	3.44	5.23	12.28	17.51
H	..	—	8.88	3.42	5.20	12.29	17.49
I	..	10.56	8.93	4.23	4.78	13.16	17.94
K	..	10.45	9.21	3.96	4.83	13.17	18.00
L	..	10.63	9.25	5.10	3.38	14.35	17.73
M	..	12.20	9.02	2.94	5.56	11.96	17.52
N	..	—	8.76	3.27	5.77	12.03	17.79
O	..	10.50	9.15	5.20	3.40	14.35	17.75
P	..	10.61	9.23	5.09	3.43	14.32	17.75

Averages.

Sample A.	Number of determinations.	Mean.	Highest.	Lowest.
Moisture 11	7.18	8.70	6.27
Soluble 15	7.08	7.46	6.63
Insoluble 15	7.55	8.04	6.40
Total 15	18.95	19.38	18.55
Sample B.				
Moisture 11	10.16	11.87	9.17
Soluble 15	10.96	11.58	10.03
Insoluble 14	3.57	3.91	3.00
Total 15	18.55	19.12	18.29
Sample C.				
Moisture 11	10.52	12.20	9.62
Soluble 15	8.94	9.25	8.67
Insoluble 15	4.75	5.77	3.38
Total 15	17.80	18.33	17.51

(To be continued.)

NOTICES OF BOOKS.

A Natural System of Mineralogy, with a Classification of Native Silicates. By THOMAS STERRY HUNT. Reprinted from "Mineral Physiology and Physiography," a Second Series of Chemical and Geological Essays. Boston: S. E. Cassino.

MINERAL taxonomy has hitherto presented difficulties which, though the subject of no little discussion, have been but very imperfectly surmounted. This want of a truly scientific arrangement showing the natural relations of species is perhaps one reason why systematic mineralogy finds at present exceedingly few followers.

Two conflicting principles have been put forward for our guidance. As most of our readers are well aware, Berzelius, as far back as 1815, proposed a purely chemical system, which has since, with certain modifications, been adopted by Rammelsberg, Naumann, Dana, and others,

and is now most generally accepted. In it the results of chemical analyses are regarded as of primary importance, whilst physical characters and crystalline form are relegated to a subordinate rank.

The opposite principle, clumsily called by Jameson the "Natural-History method," was proposed by Werner a century ago, and developed by Mohs, Breithaupt, Jameson, and Shephard. This system is based on the "natural alliances and differences which exist between minerals." Werner, it appears, pronounced the intervention of chemistry as a mere provisional expedient, and even doubted the possibility of constructing a philosophical system in which the external and the chemical characters should be co-ordinated.

We notice here an important difference in classifications. There are systems whose main object it is to admit of the easy determination of any given specimen, if possible without its destruction; and there are others which seek to show existing forms, organic or inorganic, in their natural relations and in their order of filiation.

We find that now certain ideas which have been first developed by the study of living beings are winning their way into chemistry itself. On the other hand, we recognise two very luminous principles put forward for the first time by Dr. Hunt. He shows that in the more highly-organised animals chemical considerations are of little value in taxonomy, whilst morphology is well nigh everything. In plants "characters depending upon chemical differences, such as the presence or absence of certain acids, alkaloids, and groups of essential oils," come in to aid us in determining the natural affinities of plants, whilst in simple crystals or amorphous masses morphology counts for little, and chemical considerations for almost everything. Hence the mineralogist who rejects the aid of chemistry commits a fundamental error.

As another principle Dr. Hunt compares carbon and silicon. He seems to have been the first to define organic chemistry as the chemistry of carbon and its compounds, and he might have viewed, in a like spirit, the structure of plants and animals as the "form-lore" of carbon and its compounds. In minerals silicon plays a part almost corresponding with that of carbon in the organic world.

Hence he proposes, as the base of his natural system in mineralogy, the following main principles:—

The conception of high molecular weights, like those of the carbon series in so-called organic chemistry, extended to all mineral compounds.

The conception that the laws of progressive or homologous series, previously recognised only in the hydrocarbons, are of universal application.

The conception that the variations observed in the chemical composition of mineral species are due not only to polybasic characters, but in some cases to indefinite admixtures of homæomorphous species.

The attempt to fix the molecular weights of such compounds as the polysilicates and polycarbonates from their densities, as compared with those of species the minimum molecular weights of which are otherwise determined; and the assumption that for homæomorphous solids, and probably for all solids, the molecular volumes are identical.

The adoption of atomic formulæ to represent the composition of mineral species, and the showing that comparisons of the volumes or spatial relations of complex species like the silicates, should be based on the numbers deduced from these atomic formulæ, which represent the relative volumes of the unit-weight in the species compared, P being the unit-weight got by dividing the empirical molecular weight by the number of oxide atoms in the formula (including any chloride, fluoride, or sulphide atoms which may be present), and D the specific gravity; the volume of the unit, V, is represented by $\frac{P}{D}$.

The showing that in related and homologous species

hardness and chemical indifference are inversely as V; in other words, they increase with the condensation, the relative amount of which in the species compared is shown by the diminution of V.

These principles the author works out in a classification of silicates which is here given in full.

Sozolic Acid; its Chemical, Physiological, and Therapeutical Properties. By EMILE SERRANT. Paris: Berthier.

NEW antiseptics are becoming almost as plentiful as were anæsthetics a few years ago, though there is still room for one free from the strong objections which may be urged against phenol, salicylic acid, boric acid, &c. The substance here brought before us is more strictly named orthoxyphenyl-sulphurous acid. In composition it is parallel to salicylic acid, containing, however, the group sulphuryl (SO_2) in place of the carbonyl (CO) of salicylic acid.

It is described as a reddish syrupy liquid, of sp. gr. 1.40, and having a slight odour, peculiar but not disagreeable. It dissolves in water in all proportions, congeals at 8° , and distils at 130° . With ferric chloride it gives the same violet colouration as does salicylic acid. Though a decided acid, it has not the corrosive action of phenol. It is said to arrest absolutely every fermentation, diastatic or fungoid. It is said to arrest all putrefactive changes in urine, animal refuse, sewage, the contents of cesspools to a much greater degree than do phenol, salicylic acid, &c., whilst its perfect solubility in water, its freedom from corrosive properties and from offensive odour render its employment much more convenient.

If its price permits it will doubtless meet with very extended applications.

Report on Experiments made to Test the Germination and Growth of Farm Seeds, in Mixtures of Garden Soil and Basic Cinder, from the North-eastern Steel Company, Limited. By Dr. MUNRO, F.C.S. Middlesbrough: W. H. Burnett. 1886.

IN the first part of this report Dr. Munro argues the question whether or not the presence of the protoxide of iron in the basic cinder is inimical to plant-life, as has been stated by some persons, and he concludes from his experiments that it does not interfere with the growth of plants, even when a very large proportion is present. In fact, the author found that the heaviest dressings of cinder in the 1884 and 1885 experiments—viz., 1 and 2 tons per acre—were productive of nothing but benefit.

The recent experiments were conducted in the following manner; mixtures of garden soil and basic cinder were made as shown:—

1. Pure basic cinder.
2. 50 per cent cinder and 50 per cent garden soil.
3. 25 " " 75 " "
4. 10 " " 90 " "
5. Garden soil alone.

And in pots containing each 1 lb. of these prepared soils barley, turnips, clover, mustard, and cress were sown with the following results:—The barley germinated in all the pots, but the best was in the mixture of equal parts of soil and cinder; the turnips grew in all the pots, but those in the pure cinder did not survive long; clover germinated in all, but those in the pot of equal parts of soil and cinder grew for a short time only; the mustard did best in the pure garden soil, and did not germinate in the pure cinder; the cress germinated freely in all the pots,—that in the pure cinder, however, was the poorest.

From these experiments the author concludes that seeds will develop in pure basic cinder until the store of nourishment in the seed itself is used up, but, as there is absolutely no organic matter present in the cinder to furnish nitrogenous food, the growth cannot proceed further.

Roughly speaking, two-thirds of all the seeds sown in

garden soil alone germinated, and one-half of all those sown in the mixtures germinated also; but more accurate conclusions cannot be given without having recourse to experiment on a much larger scale.

Report of the Port of London Sanitary Committee, with the Half-yearly Report of the Medical Officer of Health for the Port of London to June 30th, 1886.

THE Report deals principally with the detection of infectious diseases on board ships arriving at London, and of the means adopted to prevent the spread of such diseases. In the Introduction we find a paragraph the first part of which appears rather startling, viz., "Your officers have been greatly assisted by the continued presence of cholera on the Continent, which undoubtedly at the present time is, as it has been in the past, one of the greatest incentives to sanitary work in this country."

The subjects of inspection and report are—the Docks and River, Smallpox, Cholera, Unsound Meat, Infected Clothing, &c.; and in the Appendix are given Tables of comparison, such as the numbers of ships inspected, cases of disease found, and other information.

Taken altogether, the health of the Port of London and the sanitary precautions taken seem to be very satisfactory, when we consider the large number of vessels constantly arriving from all parts of the world, in some of which sanitation is almost unknown.

CORRESPONDENCE.

THE INTRA-ELEMENTAL FORCES.

To the Editor of the Chemical News.

SIR,—In a recent Address before the Chemical Section of the British Association, Mr. Wm. Crookes, the President, chose for his subject a consideration of the nature of our elements and their probable genesis, as well as the prospects of our dissociating them at some future time. Mr. Crookes, in an eloquent and masterly manner, called attention to the fact that our science of Chemistry rests uneasily at present concerning these so-called elements, and that it more and more loudly demands the breaking down of the barrier they present, and investigation of their composition.

I notice, however, that nothing at all was said about the specific heat of the elements, and, as it appears to me that just from this side the problem of their nature can be attacked with greater hope of success than from any other, presents, so to speak, a handle, I venture to state my ideas briefly.

Our ordinary chemical compounds have the peculiarity that their molecular heats are equal to the sum of the atomic heats of their component elements. In other words, by chemical combination the heat capacity of matter remains unchanged. Whether we take 64 grms. of a mechanical mixture of K+K+S or of the chemical compound K_2S , the heat capacity is the same. This is a characteristic of our force of chemical affinity in its action.

Looking now at the elements, we see at once how entirely different their mode of composition must be from that of our chemical compounds. The metals have all of them an atomic heat of about 6.4. That enormously heavy atom uranium has the same atomic heat as light lithium, and yet there is thirty-five times as much matter in it. Surely the component parts of uranium are united by a force acting in totally different manner from our chemical affinity, and, we may add, probably with a far superior energy. The particles of matter are by it brought so near together that the amplitudes of vibration of our heat-waves are too great to enter into their labyrinth.

Certain it is, finally, that with the decomposition of any one of our elements, answering the law of Dulong and Petit in respect of heat capacity, we will have at hand the key to an unknown land, the arena of unknown forces, beyond the surface of the element, where undoubtedly all is darkness and dead silence, and where there is neither heat nor cold, summer nor winter.—I am, &c.,

CHARLES LUEDEKING, Ph.D.

St. Louis, October, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 17, October 26, 1886.

Researches on the Decomposition of Ammonium Bicarbonate by Water, and on the Diffusion of its Components through the Atmosphere.—MM. Berthelot and André.—In nature it is generally in presence of water that ammonia and carbonic acid react upon each other in the soil, in the sea, or in the atmosphere. Experiment shows that calculations based upon the gaseous exchanges produced in the absence of a body capable of uniting with ammonia cannot be applied to the diffusion of ammonia, passing from water to air in presence of an excess of carbonic acid. The speed of the diffusion of pure ammonia is likewise very different from that of ammonia associated with carbonic acid. In presence of an excess of carbonic acid the transfer of ammonia through the atmosphere and into an aqueous liquid ensues according to laws very different from those of the transfer of ammonia in presence of an inert gas. Whilst this latter is regulated by the tension of aqueous solutions of ammonia, on the contrary, the transfer in presence of carbonic acid does not depend, at least as regards its main portion, on the tension of the total ammonia of the salt, but it depends chiefly on the comparative tension of the carbonic acid in the liquids and in the atmosphere. In a word it is the diffusion of carbonic acid which regulates the decomposition of ammonium bicarbonate by water, and consequently the transfer of ammonia.

Re-composition of White Light by the Aid of the Colours of the Spectrum.—M. Stroumbo.—The author proceeds as follows:—A spectrum is produced and projected in the ordinary manner upon a white screen by means of a prism. But care is taken to mount the prism upon an axle paralld to its edges so that it may receive a rapid rotatory movement. When the rotation is slow the seven colours are seen displacing each other upon the screen, but when the movement is rapid the colours disappear and the space swept by the movable spectrum appears like a band of white light. It is well to note that one of these extremities always remains coloured and terminates in a small stripe of pure red. This fact depends on the minimum of deviation.

Phenomena produced during the Heating and Cooling of Cast-Steel.—M. Osmond.—As the proportion of carbon increases the temperature of the transformation of iron falls. The rapidity of heating has no sensible influence on the position of the critical points. The critical points lower on cooling as this becomes more rapid. The critical points sink a little on raising the initial temperature, on setting out from which the steel is left to cool.

Saturation of Normal Arsenic Acid by Baryta-Water.—Ch. Blarez.—The heats liberated by the successive additions of mols. of baryta-water are 14, 13.5, 15.5, 0.25 and 0.50 cal. The thermic phenomena observed are not the same as those observed on neutralising

the same acid with alkalies or with calcium and strontium. The indicators, cochineal and helianthine, change colour when the saturation of the first third of the acid has been slightly exceeded. Phenolphthalein, on the contrary, reddens when two-thirds of the acid have been very exactly neutralised.

Certain Bases of the Piperidic Series.—A. Ladenburg.—The author has obtained the following bases by the transformation of pyridic bases:—Piperidine, α -methyl-piperidine (α -pipercoline), β -methyl-piperidine (β -pipercoline), $\alpha\alpha'$ -dimethyl-piperidine ($\alpha\alpha'$ -lupetidine), $\alpha\gamma$ -dimethyl-piperidine (or $\alpha\gamma$ -lupetidine), α -ethyl-piperidine, γ -ethyl-piperidine, α -isopropyl-piperidine, and γ -isopropyl-piperidine.

Bulletin de la Société Chimique de Paris.
Vol. xlv., No. 4, August 20, 1886.

Electrolysis of Coke in Ammonia.—A. Millot.—The alcoholic solution described in the author's papers (*Comptes Rendus*, August 10th, 1885, and March 15th, 1886) contains the derivatives of that substance ordinarily obtained by the action of heat, such as ammeline, biuret, and guanidine.

Action of Zinc Powder upon Benzyl Chloride.—E. Prost.—In this reaction large quantities of hydrochloric acid are evolved, and there remains a viscid mass from which the author has isolated three liquids passing over respectively at 105° to 115°, 140° to 160°, and 260° to 280°. In the latter the existence of toluene and phenyl-toluylmethane, was established, as well as of a small portion of benzyl chloride which had escaped the action of the zinc.

MISCELLANEOUS.

Society of Arts.—The first meeting of the One Hundred and Thirty-third Session of the Society of Arts will be held on Wednesday, the 17th November, when the opening address will be delivered by Captain Douglas Galton, C.B., D.C.L., LL.D., F.R.S., Chairman of the Council. Previous to Christmas there will be four Ordinary Meetings, in addition to the Opening Meeting. The following are the probable arrangements for these meetings:—Nov. 24, Wm. Anderson, M.Inst. C.E.; "Purification of Water by Agitation with Iron and Sand Filtration." Dec. 1, adjourned discussion on the paper by Dr. C. Meymott Tidy, on "Sewage Disposal" (read April 14, 1886). Dec. 8, Major-Gen. C. E. Webber, R.E., C.B., "Glow Lamps, their Use and Manufacture." Dec. 15, J. B. Marsh, "Cameo-cutting as an Occupation." There will be five courses of Cantor Lectures during the Session:—(1.) "Principles and Practice of Ornamental Design," by Lewis Foreman Day. (2.) "Diseases of Plants, with Special Reference to Agriculture and Forestry," by T. L. W. Thudichum, M.D. (3.) "Building Materials," by W. Y. Dent, F.C.S., F.I.C. (4.) "Machines for Testing Materials, especially Iron and Steel," by Prof. W. C. Unwin. (5.) "The Structure of Textile Fibres," by Dr. Frederick H. Bowman, F.L.S., F.G.S. Two Juvenile Lectures on "Soap Bubbles," by A. W. Reinold, F.R.S., will be given on Wednesday evenings, Jan. 5 and 12, 1887. The meetings of the Colonial Section and of the Indian Section will not commence till after Christmas.

MEETINGS FOR THE WEEK.

THURSDAY, 18th.—Chemical, 8. "A Spectroscopic Study of Dyes and Colours." "Note on Nægeli's Theory of Fermentation," by Prof. W. N. Hartley, F.R.S. "On the Reduction of Nitrites to Hydroxamine, by Hydrogen Sulphide," by Dr. Divers and T. Haga. "On the Preparation and Saponification of Hydrocyanides of the Diketones," by Dr. Japp and N. H. J. Miller, Ph.D.

THE CHEMICAL NEWS.

VOL. LIV. No. 1408.

THE PRODUCTION OF SOFT STEEL IN A NEW TYPE OF FIXED CONVERTER.*

By GEORGE HATTON, Bilston.

THE development of the manufacture of steel has, until recently, been almost entirely in the direction of large outputs, entailing increasingly large and costly plants; consequently the revolution from iron in favour of steel has been very severely felt by iron manufacturers, inasmuch as their existing works and plant have not been adaptable to the new order of things.

Some method of making soft steel of the highest quality, in moderate, but, at the same time, rapid and continuous quantities, and with comparatively inexpensive plant, has, therefore, long been desirable, and for this purpose, the Fixed Converter offers many advantages. The Fixed Converter is not a new invention: Sir Henry Bessemer conducted his early experiments in one, and it has been used somewhat extensively in Sweden, for many years, making steel of very high quality.

In using the old type of fixed converter, a great difficulty experienced has been the necessity for keeping the full pressure of blast on during the tapping out of the metal after the process of conversion was completed, with the risk of more or less oxidation of the bath of metal, which oxidation would, of necessity, be continued till the last of the steel ran from the converter, owing to tuyeres being fixed on a level with the converter bottom.

M. Wittnöfftt, of Bochum, Westphalia, in a paper read before the Cleveland Institute of Engineers, proposed, as a remedy for this undesirable after-blow, the employment of an auxiliary blast engine of considerably smaller dimensions than the engine used in blowing the charge, but which could be made to maintain the full pressure of blast, but with reduced volume. This smaller engine was to be started at the completion of the blow, and, at the moment of tapping the converter, the large engine being stopped, or the blast from it shut off, as soon as the smaller one was in motion. Whether this suggestion was ever put into practice or not I am unable to say.

The Clapp and Griffiths converter (a South Wales invention) was specially intended to meet this difficulty, by stopping up the tuyeres at the termination of the blow, and thus preventing further oxidation of the bath; the risk of oxidation being further minimised by fixing the tuyeres in a position about half-way between the converter bottom and the surface of the metal, so that, by the time about half the metal had left the converter, the tuyeres were free and oxidation was at an end.

The essential feature of this converter was a very ingenious arrangement for actuating the stoppers to the tuyeres. It consisted of two pistons, of unequal areas, attached to the spindle or rod carrying the stopper. The smaller piston was under the pressure of the blast during the operation of blowing, and served the purpose of holding back the stopper from the tuyere; the larger piston during that time being under atmospheric pressure only, but on the admission of the blast behind the larger piston at the end of the blow, which was done by simply opening a hand cock, the pressure on the larger area overcame the pressure on the smaller area, and the stopper was at once driven against the back of the tuyere, closing it with the exception of a very small hole provided through the centre of the stopper, which was necessary to admit sufficient

blast to keep the metal from coming back through the tuyere.

A Clapp and Griffiths converter was erected and started at the writer's works at Bilston, early in 1884, but several practical difficulties were met with, due to the construction of the converter. The position of the differential piston and stopper appliance, immediately behind the tuyere, and on a lower level than the metal line (a position of danger), was very objectionable, owing to the delay in, and costliness of, replacing them if damaged. The exposure of the back end of the tuyere, and of a large area of lining material, to the full pressure of blast in the blast box, added considerably to this danger, it being difficult to keep the lining tight, the blast having a tendency to penetrate the joints and produce outbreaks of metal into the blast box. These faults, and the general inaccessibility and immovable character of the converter lining and bottom, causing great difficulty and delay when repairs were needed, led the writer, after a short experience, to design a fixed converter upon entirely different lines, with a view to overcoming these difficulties.

A sectional elevation of this new converter is exhibited, from which its general construction will be readily understood. The whole is rigidly supported on four strong cast-iron columns, add for convenience of construction is attached to them by the blast chambers, G, which form part of the middle section of the converter shell. The lower section, C, is readily detachable, and is secured in position by cotter bolts passing through the flanges, D and E, or by other suitable means. This lower section is made sufficiently deep to enable the portion of the lining liable to the greatest wear, together with the tuyeres, to be removed with it, so that, by simply changing a lower section, in a very short space of time a converter can be completely renovated, and in this way can be kept at work night and day, almost continuously. The lining of the middle and lower sections consists principally of ganister, rammed hard, according to the usual method of lining Bessemer converters.

It has been found more convenient to line the nose, or upper section, with silica bricks, and a course of silica bricks is used at A as a support to the ganister lining of the middle section, making it safe and independent when the lower section is removed.

The tuyeres are of fire-brick, and preferably of square outer section, with a single round taper hole through the centre of each, $1\frac{1}{8}$ in. diameter at the inner end. These tuyeres are so placed as to be about 6 in. below the surface of the molten metal, and about 10 in. above the bottom. The bottom of the lower section is made with silica bricks, set in ganister, upon a bed of loam sand. One or more duplicate lower sections are provided, and as they are removed, with their linings worn out, they are repaired and placed in a stove to dry and keep warm till wanted.

The method of changing a lower section is simple; a bogie running on rails is placed under the centre of the converter, a hydraulic ram—which is actuated by a pair of manual pumps fixed any convenient distance away—then passes up through the centre of the bogie, taking the weight of the lower section, and after the cotters are removed from the bolts and the tuyere pipes disconnected, gently lowers it on to the bogie, by which means it is then removed to the repairing shed. The new lower section can now be brought into position under the centre of the converter, and raised by the ram and cottared to the middle section, the joint being made with a little plastic ganister, placed on the edge of the lower section, just before raising it into position. When the converter is blowing, the hydraulic ram is at rest, and entirely below the floor level, covered with a plate, and further protected by a bed of sand, some ten or twelve inches thick, from any possible damage from hot steel or cinder.

The blast connections to the tuyeres are so arranged that no costly valves or blast-boxes are exposed to danger behind or on a level with the tuyeres, the blast being

* Read before the British Association, Birmingham Meeting, Section B.

conveyed separately and directly from the blast-chamber, G, to the centre of each tuyere, passing through the valve, H, and down the cast-iron pipe, J, which latter has a ball and socket connection to the valve, and is held in position by a bridle, L, and set-pin, M. The lower end of the pipe at N is faced and bolted to the cast-iron tuyere block, O, which is also faced at N, and at this point a thin asbestos mill-board ring forms an air-tight joint.

When changing a lower section it is not necessary to remove the connecting pipes. They are unbolted at N, the set pins in the bridles are slackened, the pipes then swing back into an oblique position, and are there held by the bridles by re-tightening the set pins, and in this position are out of the way of the lower section.

The valves, H, are of the ordinary baffle type, are all connected together by levers, and can all be closed or opened by the movement of one handle.

Each valve has a hole $\frac{1}{2}$ inch diameter, through which sufficient blast passes while the valve is closed to support the weight of metal in the converter, and keep it out of the tuyeres during the process of tapping. The nose of the converter is accessible from an upper platform, and a movable spout is provided for the purpose of charging scrap during the blow.

The charge is run direct from a cupola, and consists of about 46 cwt. of hæmatite iron, the blast being put on at the converter at the moment the cupola is tapped. The blow usually lasts about fifteen to eighteen minutes, and just as the carbon blow is commencing, most of the silicon being by then eliminated; a greater portion of the slag is allowed to boil out at the slag-hole provided at S; this lasts about one to two minutes, when the hole is stopped up for the remainder of the blow. The charge is blown right down,—that is, till the carbon flame has disappeared,—when the signal is given to tap out; at this moment the valves are closed, and the steel instantly begins to run from the tapping spout. Ferro-manganese, finely crushed, is added in the ladle while the steel is running from the converter, in about the proportion of 20 lbs. per ton (for 80 per cent manganese). The quantity of steel produced per blow is about 2 tons.

The pressure of blast used may be from 5 to 8 lbs. per square inch; in no case need it ever exceed about half that required in the ordinary Bessemer process, or say 10 lbs. as a maximum.

The rapidity with which the converter can be worked depends very much upon the facilities at hand for dealing with the steel produced.

At the writer's works, twenty blows per shift of twelve hours have been done, but, with more efficient casting-pit arrangements, this output could be very considerably increased.

The usual numbers of Bessemer hæmatite pig iron are used, the percentage of silicon preferred in the mixture being about $1\frac{1}{2}$ to 2 per cent. When working rapidly, with surplus heat, a considerable quantity of scrap is added through the nose during the blow.

The steel produced by this process is of the highest quality, remarkably soft, and particularly adapted for welding, it being largely in demand for lap-welded boiler tubes and other similar purposes; it is also made into boiler plates, and is largely made into stamping sheets and tin plates for difficult work. Samples of it are to be seen at the Bingley Hall Exhibition.

The carbon is exceedingly low, averaging from 0.05 to 0.10 per cent, and seldom exceeding 0.15 per cent.

The silicon seems to be more thoroughly removed than in the Bessemer process, which is a great advantage, and is probably due to the less acid character of the slag at the end of the blow, resulting from the removal of the greater portion of the silicious slag at the end of the silicon blow as already described, the following being the analysis of the slag at the termination of the blow:—

FeO.	SiO ₂ .	MnO.	Al ₂ O ₃ .
41.90	46.22	6.97	4.89

The tensile strength of the steel is about 24 to 26 tons per square inch, with elongations averaging 25 per cent. Some analyses are as follows:—

C.	Si.	S.	P.	Mn.
0.04	trace	0.07	0.06	0.30
0.07	0.009	0.02	0.05	0.37
trace	0.008	0.05	—	0.30

The advantage claimed for the process over the ordinary Bessemer process, apart from the question of cost of outlay, is that a better quality is produced—one that is uniformly softer and more reliable; the reason for this being that the action in the converter is less violent. The charge can always be blown right down, with less risk of oxidation, owing to the fact that the final changes take place less rapidly: this is due to the low pressure of the blast, and to the fact that instead of the whole charge being constantly penetrated and oxidised by direct contact with the blast, as is the case in the ordinary bottom-blown Bessemer converter, only about a third of the charge is subject to direct oxidation at any one time, a further indirect process of oxidation at the same time being carried on by circulation and admixture of the oxidised iron with the remaining portion of the bath.

Further, by tapping the steel from the bottom of the charge, all risk of taking up particles of partially converted metal, which may adhere in and around the nose, and contain more or less silicon, is avoided, as is also all unnecessary contact with slag, which remains on the top of the bath, and only runs from the converter after the steel is in the ladle.

Some advantages of this process, compared with the Siemens process, are that—where only a moderate output of steel is required—the constant and regular production of ingots enables soaking pits to be economically used, instead of the more costly method of heating in furnaces. Also, softer material (lower in carbon) can be made with regularity and certainty; also, Welsh or other hæmatites made from Spanish ore, containing a larger percentage of manganese than West Coast brands, can be used with great advantage,—in fact, are preferred,—and when not used alone are almost always used as a mixture with West Coast iron.

This converter is well adapted for making steel castings. Though the plant at the writer's works has not been designed with that view, castings, weighing from a few pounds to upwards of one ton each, have been repeatedly made, and always with success. The following are analyses of some of them, which, though rather variable, the castings were all sound and satisfactory:—

C.	Si.	S.	Mn.
0.16	0.113	—	0.18
0.50	0.30	0.027	0.99
0.42	0.046	0.04	0.46
0.66	—	—	0.50
0.28	0.181	—	—

ON THE DETERMINATION OF ALUMINIUM IN PRESENCE OF LARGE PROPORTIONS OF IRON.

By ROBERT T. THOMSON.

HAVING lately had occasion to test for and determine a minute proportion of aluminium in presence of a large proportion of iron, I was led to try the capabilities of the two best-known methods, namely, by boiling with a large excess of caustic soda or potash and subsequent precipitation in the filtrate from the peroxide of iron, and by direct precipitation with thiosulphate of sodium. In the latter case only about 90 per cent of the total aluminium present was obtained, when working on a solution containing 100 parts of iron to 1 part of aluminium. But

the failure of the caustic alkali method was more striking, as not a trace of alumina could be detected in the soda filtrate. The solution operated upon contained 2 grms. of iron and 0.02 gm. of aluminium. It was nearly neutralised, and slowly added to a quantity of caustic soda solution heated to boiling in a nickel basin. The mixture was thoroughly boiled, filtered, and tested for alumina, with a negative result, as already stated. The excess of caustic soda used was more than 10 grms. Both of these processes had to be rejected, but I at last hit upon the following method, which gives excellent results:—

The iron, if in the ferric state, is first reduced to the ferrous condition by passing a current of sulphurous acid through the solution. The excess of sulphurous acid is boiled off, the mixture cooled, and at least as much phosphoric acid, or phosphate of ammonium or sodium, added as will be equivalent to the alumina present. It is advisable to use a large excess of phosphoric acid, as the alumina may not be completely precipitated if it has not at least its own equivalent of the former. One drawback to the unlimited use of phosphoric acid is that if manganese is present it will be thrown down, but if the quantity of the former is limited the latter will remain in solution. Where manganese is present in quantity it is advisable to employ the alternative method of precipitation to be described further on. Ammonia is now added until a faint permanent cloudiness is formed; then excess of ammonium acetate, which throws down the alumina as phosphate. The precipitate always contains some ferric phosphate, which forms from any traces of ferric iron salt which may have escaped reduction, and from the oxidising action of the air during filtration. The great bulk of the iron, however, remains in solution in the ferrous condition. The precipitate is now collected on a filter, washed two or three times with water, and dissolved by passing dilute warm hydrochloric acid through the filter. If it does not seem sufficiently free from iron, the solution thus obtained should be put through the same process as has been just described, beginning at reduction with sulphurous acid. When filtered rapidly I have had as little as 0.1 gm. of peroxide of iron in the aluminium phosphate, and in no case have I required a re-precipitation. It is well to reduce the iron as much as possible.

An alternative method of getting rid of the great proportion of the iron is to add ammonia to the reduced solution till a slight cloudiness is formed; then excess of ammonium acetate, and boil for a few seconds. The whole of the alumina and a portion of the iron are precipitated, and are collected on a filter. No phosphoric acid is added in this case, and manganese remains in solution. More iron is brought down than in the first-described cold method, and, when only minute quantities of alumina are expected, a second reduction and precipitation will most likely be necessary.

After obtaining a satisfactory precipitate (whichever method has been adopted) it is dissolved in hydrochloric acid, boiled with a little nitric acid to oxidise any proto-salt of iron, nearly neutralised with pure caustic soda, and added to a considerable excess of the latter in a nickel basin. The mixture is boiled for a short time, filtered, the filtrate acidified with hydrochloric acid, and a large excess of phosphoric acid or phosphate of ammonia or soda added. I have found that the presence of at least two equivalents of P_2O_5 to one of Al_2O_3 are necessary to give rise to the normal phosphate of aluminium ($Al_2P_2O_8$). The latter is now precipitated by adding ammonia till a slight cloudiness is produced, and then excess of acetate of ammonium. Or the precipitation may be effected by simple neutralisation with dilute ammonia till a red reaction ceases to be obtained with blue lakmoid paper. The aluminium phosphate is now collected on a filter, washed thoroughly with a hot 1 per cent solution of ammonium nitrate, containing about 0.1 gm. of the di-acid ammonium phosphate ($NH_4H_2PO_4$) per litre, dried, ignited, and weighed. If the aluminium phosphate is washed with water it partially loses its gelatinous form,

and becomes tedious to filter. But besides this the precipitate is decomposed to a considerable extent, and a portion of the phosphoric acid passes into solution. For these reasons the precipitate must be washed in the manner described, when pure $Al_2P_2O_8$ is weighed, and may be calculated to alumina or aluminium as required.

The following are results obtained by the above process in solutions containing 3 grms. of metallic iron. To the iron solution a weighed quantity of pure ammonia alum was added.

Grm. of Al_2O_3 added.	Grm. of $Al_2P_2O_8$ obtained.	Grm. of Al_2O_3 obtained.
0.0340	0.0800	0.0336
0.1135	0.2695	0.1132
0.1135	0.2703	0.1136

The presence of titanium is not injurious in the above process, as only slight traces of titanous acid are dissolved by strong caustic soda.

City Analyst's Laboratory, Glasgow.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 244.)

6. *Attacking and Dissolution of Minerals.*

To dissolve the powdered mineral we make use of fuming hydrofluoric acid (2 or 3 c.grms. of acid to 0.5 m.grm. of material) or fluoride of ammonium combined with hydrochloric acid. It is necessary to make sure that the hydrofluoric acid is quite free from sodium, calcium, and aluminium, by evaporating to dryness 1 c.c. of the commercial acid with several centigrammes of sulphuric acid, and then making an analysis of the residue. Even if the acid is impure it can still be very well used for preparing fluoride of ammonium. Commercial hydrofluoric acid always leaves a slight residue when evaporated to dryness, even when it contains no salt in solution: this residue, which is of a brown colour, is carbonised by the addition of sulphuric acid; it comes from the fact that the acid is always kept in gutta-percha bottles.

If this residue, which under the microscope appears as little brownish black flakes, interferes too much, we can use instead the mixture of fluoride of ammonium and hydrochloric acid. The action of this mixture is not so energetic as that of fuming hydrofluoric acid, and we must be careful, when trying for potassium, to increase the temperature to a red heat after the evaporation.

The same difficulties occur when we try to keep a stock of these reagents. We can only use platinum or gutta-percha bottles for this purpose, and gutta-percha bottles large enough to carry any considerable quantity are very awkward to manipulate when we only require a few centigrammes of the acid. The most convenient form of flask is about 30 c.c. capacity: in the stopper is fixed a little gutta-percha or platinum wire, twisted into the form of a corkscrew; this screw is about 3 m.m. in diameter, and serves as a sort of pipette. It is not easy to procure these bottles, and even less easy to make them in the laboratory. We can make gutta-percha receptacles for keeping fluoride of ammonium by taking a lump of gutta-percha which has been softened in warm water, and squeezing it in between two porcelain crucibles of the shape we require. The porcelain crucibles must be oiled first to prevent the gutta-percha from sticking to them. The lid is formed in the same manner, between two porcelain lids, one of which has had the handle broken off. The best way of conducting the attack with hydrofluoric acid is in a hemispherical cup of platinum about 1 c.m. diameter, such as are used for blowpipe experiments.

To clean these platinum cups we must make a mould

by turning out a little cavity, of the same shape, in a block of box-wood; or we can make one quite as effectively with plaster-of-paris and a solution of lacquer in alcohol.

These moulds serve as supports, and enable us to clean the cup thoroughly without any risk of damaging them.

Concave dishes for sublimation can be made by hammering thin plates of platinum which have been heated to redness until they take the required form. It will be found most convenient to use a piece of lead as an anvil, and a hammer similar to those used for making cupels.

When we have to deal with a silicate we commence by placing a few drops of hydrofluoric acid, or fluoride of ammonium and hydrochloric acid, into the crucible; then we add the powdered mineral. We evaporate at a moderate heat, and if necessary we add a little more of the reagent and evaporate afresh. In this operation, as well as in those which will be described later on, great care must be taken with regard to the hydrofluoric acid fumes, as a very small quantity may cause severe results if in contact with any wound.

To the dry residue, which consists of fluorides, we add sulphuric acid, diluted so that abundant vapours of concentrated acid are given off after a prolonged evaporation. This operation must be performed with great care, so that there remains no fluosilicate or fluoaluminate unattacked. It is as well not to drive off all the sulphuric acid; a slight excess helps the solution of the salts in water, and sometimes it even aids the formation of crystals; it also prevents the inconvenient drying up of drops during the microscopical examination.*

Thus in cases of necessity we have to add a little sulphuric acid and re-evaporate, until the vapours commence to come off, before proceeding to dissolve in boiling water. Then we fill the cup half full of water, and evaporate the contents by boiling gently until there remains only about 1 c.grm. of the solution for every 0.1 m.grm. of mineral.

7. Test for Calcium.

The solution of sulphates must be introduced into a capillary tube about 2 m.m. diameter, which serves as a pipette. By blowing cautiously in the end of the tube we can manage to get on a glass plate several drops of about 2 or 3 m.m. diameter. The capillary tube enables us to divide the material under examination into several portions, even when it does not weigh more than 0.1 grm. We can also keep prepared solutions therein for an indefinite period.† The glass plate carrying the drops is placed, without any cover, under a microscope magnifying about 150 or 200 times. I prefer working without a cover, and I protect the object-glass by means of a thin plate of mica fixed with a little glycerin, because the evaporation of the drop has sometimes been of very great service, and the action of the reagents is much more rapid and even than when a cover is used.

If the mineral contains a sensible quantity of calcium we see, either at once or after the lapse of two or three minutes, crystals of gypsum of the well-known form, $\infty P, P, \infty P, \infty$. If the quantity of calcium is considerable the field of observation is filled with short rudimentary prisms, characteristic of gypsum: between these crystals fine needles are formed, often grouping themselves together in irregular rosettes. The transverse measurement of these crystals is still smaller when the solution contains much hydrochloric acid.

Later on we see larger crystals appear on the margin of the drop, whose angles we are able to measure, and amongst which we sometimes find twin lance-heads. The gypsum crystals are generally about 60 microns in length and 6 microns wide.

It is only very rarely necessary to hasten the crystallisa-

* If we want to keep any specimens for some time, we can prevent evaporation by adding a little glycerin and covering it over. If the evaporation has been carried too far, we can remedy it by breathing gently on the dried mass, or by adding a small drop of water with a platinum hook.

† If we leave a capillary tube in a vertical position for several hours the solution becomes perfectly clear.

tion with alcohol. We, however, when this is advisable, place the plate for a few minutes in a cardboard box, which has been wetted with alcohol. The crystals obtained in this manner resemble those formed in a hydrochloric acid solution after the addition of sulphuric acid.

In the greater number of cases we can get very fair results by evaporation only; I once obtained crystals, after waiting some time, and without the aid of alcohol, from a solution containing only 0.3 per thousand parts of lime.

The sensitiveness of this reaction is quite sufficient; in fact, it is possible to detect the presence of 0.0005 m.grm. of lime. This sensitiveness is quadrupled by the aid of alcohol; but, as I have already remarked, it is at the expense of size and sharpness of form of the crystals.

Experiments with the more common reagents, such as ammonium oxalate, oxalic acid, and ammonium carbonate, are not satisfactory. The crystals of the oxalate and carbonate are too confused and small, unless we are willing to devote a very much longer time to the experiment.

(To be continued.)

TESTING ANALYSTS.

REACTIONS useful in the examination of some novel substance, natural or artificial, are often wanted and often found. But never till lately did we hear of a proposed test for analysts. Unfortunately the rationality of the proposal is by no means on a par with its novelty. As we learn from the *Times* of the 10th inst., Councillor Taylor, of Bedford, who is, forsooth, a member of the "Food and Drugs Committee," made a statement which the leading journal rightly calls "extraordinary." He is reported to have said that during the month six samples of beer had been sent to Guy's Hospital for analysis, and he, in the presence of a chemist, saw placed in one of the samples a large quantity of a most deadly poison. "This," said Mr. Taylor, "was done because he considered that not only should the analyst test their drugs, but the analyst ought himself to be tested." The report upon this sample was as follows:—"I am of opinion that the sample of beer is genuine."

Now we have no right to say that this "test" was purposely concocted to bring the analyst concerned and analytical chemistry in general into disrepute. But if it was an honest *bona-fide* attempt on the part of Councillor Taylor to try the trustworthiness of the analyst, it shows a lamentable want of judgment and of common sense. An analyst, on receipt of a sample, does not proceed to examine it for every known substance. Were he required to do so the fee which he would necessarily have to demand would, perhaps, astonish the Bedford Food and Drugs Committee. As the matter is ably put by Dr. W. H. Corfield in the *Times* for the 11th inst.:—"When a sample of food is sent to a public analyst for analysis it is presumed by him to have been bought in the ordinary course of trade, and he, therefore, only examines it for substances which his experience teaches him are to be found in adulterated samples of that kind of food."

Further, according to all accepted definitions of adulteration, the beer, though poisoned, was yet "genuine." By adulteration is understood, not the addition to saleable articles of any substance whatever, but the addition of foreign matter in order to increase quantity, to render the quality seemingly better than it really is, to mask defects, &c. The addition of a "most deadly poison" which answers none of these purposes, is not "adulteration," but a totally distinct and a much more serious crime.

We do not know whether municipal officials are acting within their legal competence in tampering with samples taken for analysis,—a point upon which we should recommend the Society of Public Analysts to obtain an authoritative opinion. But we submit that a safer and a more rational method of "testing the analyst" would

have been to add to the beer some substance which is known to be used, or at least to have been used, in the sophistication of malt liquors, and see whether chemical analysis be able to detect the fraud.

Since writing the above remarks we have met with three letters upon the subject in the *Times* of the 15th instant, which demand notice. The first of these communications, signed by Messrs. Bernard Dyer and Otto Hehner on behalf of the Society of Public Analysts, takes the same view as that of Dr. Corfield and our own, —namely, that a Public Analyst in his official capacity is merely bound to search for substances added for the purposes of sophistication, and not for the detection of "deliberate attempts at poisoning." From this letter, and from the concluding sentence of the one by the Public Analyst for Bedford, we judge that Mr. Taylor's "ridiculous trick" is a violation of directions laid down in the statute. Whether persons tampering with samples taken incur any legal penalty it is not our province to decide.

The town-councillor in question writes in an impenitent vein. He thought it part of his duty to see that the rate-payers "were really having the thorough analysis for which they are called upon to pay at the rate of a guinea per sample." Now the analysis which a Public Analyst is called upon to perform merely extends to the detection of such adulterants as are known to be in use. He admits that "an analyst would not be expected to test for anything foreign in the adulteration of the article," but he seeks to evade this point by adding that "he" (doubtless his confederate in the trick) "had the fairness to select a poison *well known in the adulteration of beer.*" These last words are painfully ambiguous. Does Mr. W. E. Taylor mean to say "well known to be at present used in the adulteration of beer"? Numbers of poisons have been *alleged* to be used in the adulteration of beer without satisfactory evidence. If the analyst has to search for the whole number his "guinea" will be indeed hard-earned.

The Public Analyst for Bedford writes that one of his assistants was apparently made ill by tasting the samples. He informs us, further, that the Town Clerk of Bedford has so far not complied with his urgent request for full particulars.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 4th, 1886.

W. CROOKES, Esq., F.R.S., Vice-President, in the Chair.

MESSRS. H. Crompton, G. Dyson, T. B. Tyson, and S. Williamson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James A. Audley, Ladderedge, Stoke-on-Trent; Chichester A. Bell, B.A., 54, Warwick Gardens, Kensington, W.; John Williams Bevan, Southview House, Shirehampton, N. Bristol; William Beecroft Bottomley, 26, Thorngate Road, Paddington; Cuthbert Robert Blackett, Fitzroy, Melbourne; Ebenezer John Cox, 23, Albany Road, Harborne, Birmingham; John Fuller, Rookwood, Chapter Road, Willesden Park; Alexander Galt, 61, Sardinia Place, Hillhead, Glasgow; Thomas Forrest Garvin, Colombo, Ceylon; Henry John Hardy, 163, Edmund Road, Sheffield; Sydney Joseph Harris, Wedgewood Institute, Burslem, Stoke-on-Trent; George Crompton Holt, Green Bank, Lawton, Kids Grove, Stoke-on-Trent; H. E. Kirby, Kelsey Park, Beckenham, Kent; Henry A. B. Leissner, 8, Loftus Street, Sydney, N. S.

Wales; Walter Leach, 27, St. Andrew's Place, Bradford; Hugh O'Donaghue Macan, B.A., Park Villa, St. Leonard's Road, Exeter; James B. L. Mackay, Trinity College, Melbourne; James B. Mackintosh, School of Mines, New York; Edward Lloyd Marks, Melbourne; Mu N. A. F. Moos, Poona, India; Herbert Pilkington, Tipton Green Furnaces, Tipton; L. S. M. Pyke, Devonshire Place House, Regent's Park, N.W.; Edwin Guayle, Glebe Point, Sydney; James Schleselman, Dundee; Harry Silvester, Roskhdyn, Broughton, Wrexham; Joseph Stapleton, 3, Lower Sackville Street, Dublin; Alfred Hughes Twining, Salcombe, Knightsbridge, Devon; Arthur Turner, The Limes, Aylesbury; William Walker, Junr., Saltburn-by-the-Sea; Reginald Williams, The Green, Norton, Stockton-on-Tees.

The following papers were read:—

86.* "*The Action of Chlorosulphonic Acid on Naphthalene- α - and β -Sulphonic Acids.*" By HENRY E. ARMSTRONG and W. P. WYNNE, B.Sc.

The investigation recorded in this paper is an extension of that of Armstrong and Graham on the action of sulphuric acid on naphthalene (*Trans.*, 1881, 133; *Ber.*, 1882, 204). The separation of the products of the action of sulphuric acid proving a matter of great difficulty, it was judged expedient to postpone their study until further knowledge of the naphthalenedisulphonic acids had been obtained, and with this end in view such acids have been prepared by reactions in which the possibility of secondary changes taking place, such as readily occur on heating with sulphuric acid, is reduced to a minimum.

When naphthalene and SO_3HCl react in the proportion of molecule to molecule, naphthalene- α -sulphonic acid is alone produced; it is therefore only necessary to use double this proportion of chlorosulphonic acid, and the operation becomes equivalent to that of sulphonating the α -monosulphonic acid. It is desirable to add a slight excess of SO_3HCl , as some disulphochloride is formed; the naphthalene may be dissolved in CS_2 , which is subsequently distilled off on the water-bath, or the chlorosulphonic acid may be added directly to the naphthalene. No higher acid is formed, even when a considerable excess of SO_3HCl is used, at temperatures not exceeding 100° . To isolate the disulphonic acid, the product is neutralised with lead carbonate, and the dried and finely divided lead salt is exhausted with hot spirit; the portion thus extracted is lead naphthalene- α -sulphonate; the residue consists of the disulphonate.

The acid thus prepared—no evidence of the presence of isomers has been obtained—differs from the two disulphonic acids of Ebert and Merz; its (sulpho) chloride melts at 184° , and on treatment with PCl_5 yields γ -dichloronaphthalene (Armstrong and Graham), so that the acid is probably the $\alpha^1\alpha^4$ modification. It may be termed γ -naphthalenedisulphonic acid. The lead, calcium, and barium salts very closely resemble the corresponding salts of Ebert and Merz's β -acid, which there is reason to believe is the symmetrical or $\beta^2\beta^3$ modification, dissolving very sluggishly in water, and parting with their water of crystallisation only at a high temperature and slowly. The potassium and sodium salts (each containing 2 mols. Aq.) crystallise well, especially the latter, which forms glistening well-defined plates; although easily soluble in water, they are less soluble than the same salts of Ebert and Merz's α -acid.

Naphthalene- β -disulphonic Acid.—This acid appears to be the sole product of the action of SO_3HCl on potassium naphthalene- β -monosulphonate. The chloride is added in the proportion of 3 mols. to 1 mol. of the dry salt, it being advantageous to employ a considerable excess of SO_3HCl in order to obtain a liquid product, and finally heat is applied by means of a water-bath; as a rule it is only necessary to heat during a few minutes to ensure

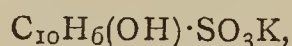
* Communications 86 to 91 are Nos. 1 to 6 from the Chemical Department of the City and Guilds of London Institute Central Institution, South Kensington.

the whole of the salt being attacked. More or less sulphochloride is formed, the amount depending on the time during which heating takes place. Water is cautiously added to the product, and the acid potassium sulphate which separates after a time is filtered off; the remaining dissolved sulphate is separated by evaporating on the water-bath and adding spirit to the residue.

The barium salt, $C_{10}H_6(SO_3)_2BA + 4OH_2$, and the potassium salt, form granular masses very similar to the corresponding β -monosulphonates in appearance and solubility; the sodium salt, $C_{10}H_6(SO_3Na)_2 \cdot 7OH_2$, forms long needles, very soluble in water. The sulphochloride is very soluble in benzene, but crystallises well from a mixture of benzene and shale spirit in aggregates of short prisms, and melts at $128-129^\circ$.

87. *The Action of Bromine on (Schaefer's) Betanaphthol-sulphonic Acid.* By HENRY E. ARMSTRONG and F. W. STREATFEILD.

As end product of the action of bromine on



Armstrong and Graham obtained a yellow salt of the formula $C_{10}H_4BrSO_6K$, and from the manner in which it was produced they were led to regard it as a *bromoxynaphthaquinonesulphonate*, $C_{10}H_4(O_2)(OBr) \cdot SO_3K$, rather than as a *naphthaquinonebromohydroxysulphonate*, $C_{10}H_3Br(O_2)(OH) \cdot SO_3K$; a small quantity of a yellow crystalline body was produced simultaneously but was not examined.

The authors have further studied these products. On adding barium chloride to a boiling solution of the potassium salt, a garnet-red salt crystallised out, which after dehydration contained 29.18 per cent barium, corresponding with the formula $C_{10}H_3BrSO_6BA$; on treatment with acid this is converted into a yellow monobarium salt, $(C_{10}H_4BrSO_6)_2Ba$. The production of these two salts leaves no doubt that the potassium salt is a *naphthaquinonebromohydroxysulphonate*.

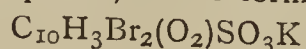
The yellow by-product is found to be *dibromohydroxynaphthaquinone*, $C_{10}H_3Br_2(O_2) \cdot OH$.

The authors have discovered tetrabromonaphthol to be a (third) product of the action of bromine on Schaefer's salt. They find also that it is possible to prepare what appears to be a tribromonaphtholsulphonate by the action of bromine on potassium betanaphtholsulphonate dissolved in boiling muriatic acid. By oxidation of Schaefer's acid they have obtained a sulpho-acid—probably β -sulphophthalic acid: the experiments were made before the publication of those of Graebe and Rée, and it remains to identify the oxidation product with the β -sulpho-acid described by these chemists; the results, however, serve to confirm those of Claus and leave no doubt that Schaefer's acid is a *heteronuclear* di-derivative of naphthalene.

88. *The Action of Bromine on the Naphthalenesulphonic Acids.* By HENRY E. ARMSTRONG and W. P. WYNNE, B.Sc.

As a general result of their experiments, the authors conclude that all the *heteronuclear* naphthalenesulphonic acids, or heteronuclear naphthalenesulphonic-derivatives, yield as end product, on treatment with bromine, a bromine-derivative of either naphthaquinonesulphonic acid, or of naphthaquinone.

From the potassium salt of Ebert and Merz's β -disulphonic acid they have obtained a salt crystallising in well-defined yellow plates, of the formula



(found $K = 8.69$, $Br = 37.05$; theory $K = 8.98$, $Br = 36.87$). The α -salt of these chemists yields what appears to be an isomeric dibromonaphthaquinonesulphonate, crystallising in very soluble pale yellow needles (found $K = 8.63$).

Potassium naphthalene- β -monosulphonate is first converted into the dibromosulphonate described by Jolin; on further treatment this yields what appears to be a

tetrabromonaphthalenesulphonate, a brominated quinonesulphonate and tetrabromonaphthaquinone.

The authors' β -disulphonate is first converted into a dibromomonosulphonate isomeric with that prepared from the β -monosulphonate; on further treatment this yields the same product apparently as Jolin's isomeric salt.

Potassium naphthalene- α -monosulphonate is known to yield dibromonaphthalene (m. p. 81°) as chief product on bromination. From their γ -disulphonate the authors have obtained a dibromomonosulphonate, two salts—each of which gives results on analysis indicating that they are dibromoquinonesulphonates, dibromonaphthaquinone, and a substance which appears to be hexabromonaphthalene; these two last are the chief products.

Hence it appears that an α -sulphonic radicle is readily displaced by bromine, but that a β -sulphonic radicle resists displacement (probably) until the nucleus in which it is contained undergoes oxidation.

89. *" α -Nitro-, α -Bromo-, and α -Chloronaphthalene sulphonic Acids."* By HENRY E. ARMSTRONG and S. WILLIAMSON.

As such different results are obtained on sulphonating naphthalene under various conditions, it appeared desirable to acquire further information regarding the behaviour of naphthalene-derivatives towards sulphonating agents.

α -Nitronaphthalenesulphonic acid has been prepared by Clève from nitronaphthalene and fuming sulphuric acid; it corresponds to γ -dichloronaphthalene, and is therefore, in all probability, the $\alpha^1\alpha^4$ modification. The authors find that the same acid may readily be prepared by means of ordinary sulphuric acid, or by the action of SO_3HCl ; they have not met with an isomer. The potassium salt is remarkably stable in presence of bromine, and no well-defined product is obtained by heating an aqueous solution with bromine at 100° ; but on evaporating the resulting yellow solution a deep purple-red coloured liquid is obtained. On distilling the potassium salt with $K_2Cr_2O_7$ and muriatic acid, a mixture of almost colourless chloronitronaphthalene (m. p. 111°) with a dichloronitronaphthalene (m. p. 85°) passes over; a dibromonitronaphthalene is formed on similar treatment with $K_2Cr_2O_7 + HBr$.

When bromonaphthalene is sulphonated by means either of H_2SO_4 or SO_3HCl , it yields together with $\alpha^1\alpha^4$ $C_{10}H_6Br \cdot SO_3H$, which is already well known and is the chief product, an isomeric acid, the salts of which are much more soluble than those of the 1:4 acid; the chloride of this acid crystallises from benzene in long prisms melting at 151° .

Chloronaphthalene in like manner yields a small amount of an isomer of the 1:4 acid when sulphonated by SO_3HCl ; the salts of the new acid are easily soluble; its chloride crystallises from a mixture of benzene and shale spirit in clusters of short thick prisms melting at 127° .

1:4 Chloronaphthalenesulphonic acid is readily attacked by bromine, and the 1:4 bromo-acid by chlorine ($K_2Cr_2O_7$ and HCl), both yielding the 1:4 bromochloronaphthalene (m. p. 67°) described by Guareschi.

On treatment with bromine, 1:4 bromonaphthalenesulphonic acid is for the most part converted into 1:4 dibromonaphthalene (m. p. 81°), but this is not the only bromonaphthalene produced; moreover, a portion is converted into a quinonesulphonate such as is referred to in the preceding note.

90. *The Hydrolysis of Sulphonic Acids.* By A. K. MILLER, Ph.D.

On page 93 of this year's *Berichte*, Kelbe states that the method of hydrolysis described by Professor Armstrong and the author (*Trans.*, 1884, 148), yields unsatisfactory results, especially when applied to the decomposition of bromotoluenesulphonic acid and similar compounds. He introduces a modification consisting in the employment of superheated steam, which, he maintains, so far improves the method that excellent results are

obtained even with the sulphonic acids of brominated hydrocarbons. The author describes experiments on the recovery of orthobromotoluene from its sulphonic acid, the results of which show that Kelbe's modification is a complication rather than an improvement, the percentage yield of bromotoluene when steam at 100° was employed being equal to the percentage yield in the experiments described by Kelbe.

91. "The Action of Bromine on Toluene-*parasulphonic Acid*." By the same.

The bromotoluenesulphonic acid used in the experiments mentioned in the previous notice was prepared by heating an aqueous solution of potassium toluene-*parasulphonate* with bromine. Potassium orthobromotoluene-*parasulphonate* [$\text{CH}_3 : \text{Br} : \text{SO}_3\text{K} = 1 : 2 : 4$] was found to be the chief product, but besides this parabromotoluene and parabromobenzyl bromide were obtained, together with an oil which is thought to be orthoparadibromotoluene, and a solid substance melting at about 250°, the composition of which has not yet been determined.

DISCUSSION.

DR. PERKIN remarked that a method capable of yielding a pure bromo-derivative such as orthobromotoluene would be of value; he had recently prepared bromobenzene from aniline by Sandmeyer's process, and had found that it contained a sufficient amount of impurity to affect its physical properties.

Dr. ARMSTRONG said that the orthobromotoluene obtained by Dr. Miller had a constant boiling-point. He would recommend Dr. Perkin to prepare bromobenzene in the ordinary way, to sulphonate it and purify by means of one of the salts, and then recover it by hydrolysis.

92. "Phosphorus Tetroxide." By T. E. THORPE, F.R.S., and A. E. TUTTON, Associate of the Normal School of Science, South Kensington.

The authors have examined the product formed by combustion of phosphorus in a limited supply of air, with especial reference to the statements of Reinitzer (*Ber.*, 1881, 14, 1884) that when dissolved in water, under certain conditions, it gives a solution of a light-yellow colour, and that after dialysis this liquid is found to contain a body of perfectly neutral reaction, and coagulates on being heated to 80° after addition of a few drops of mineral acid.

The authors, having repeated Reinitzer's experiments, are unable to confirm the existence of this so-called colloidal modification of phosphorous oxide. The yellow colour of the solution is due to the presence of the phosphorous suboxide of Le Verrier as an extremely finely divided powder, which can be removed from the liquid by repeated filtration. The colourless solution has a strong acid reaction, shows no turbidity on heating to 80°, and gives all the reactions of phosphorous acid.

When the mixed products of combustion of phosphorus are heated *in vacuo* to about 290–300°, phosphorus suboxide is formed, together with a sublimate of colourless, transparent, rhombic crystals.

These crystals sublime *in vacuo* at 180°, and are extremely deliquescent; they dissolve in water with formation of a solution of orthophosphoric and phosphorous acids, and on analysis give numbers agreeing with the formula P_2O_4 . From the mode of action of water upon it, which is analogous to that of water upon N_2O_4 , the authors are inclined to believe that this substance is the true tetroxide of phosphorus, and not the anhydride of the so-called phosphorosulphuric acid, or hypophosphoric acid, discovered by Salzer.

93. "Conversion of Ditolane-azotide into Diphenanthrylene-azotide." By FRANCIS R. JAPP, F.R.S., and COSMOS INNES BURTON, B.Sc.

In a previous communication on the ammonia-derivatives of benzoïn (*ante*), Japp and Wilson showed that the so-called "benzoïnimide" of Erdmann, to which this author assigned the formula $\text{C}_{14}\text{H}_{11}\text{N}$, had in reality

the formula $\text{C}_{28}\text{H}_{20}\text{N}_2$. They proposed to call it *ditolane-azotide*, and regarded it as an analogue of diphenanthrylene-azotide, $\text{C}_{28}\text{H}_{16}\text{N}_2$. A confirmation of this view would be found, if it were possible to convert the two tolane-groups in ditolane-azotide into two phenanthrylene-groups and thus obtain diphenanthrylene-azotine. Following the analogy of Graebe's synthesis of phenanthrene from stilbene, the authors therefore passed the vapour of ditolane-azotide through a red-hot tube; but only a small quantity of tarry product was obtained. However, by passing the vapour of the compound over heated soda-lime a distillate was obtained, from which diphenanthrylene-azotide, with all its characteristic properties, could be isolated. This result was confirmed by the analysis of the compound.

94. "A Chemical Study of Vegetable Albinism." Part III. *Experiments with Quercus rubra*." By A. H. CHURCH, Professor of Chemistry in the Royal Academy of Arts.

In previous papers (*Trans.*, 1879, 33; 1880, 1) the author has called attention to conspicuous chemical differences between the white and green foliage of seven distinct plants; in the present communication he describes the results of his study of the foliage from a large albino bough on a fine and old specimen of the scarlet oak of North America in the Royal Gardens, Kew, pointing out that they confirm and extend his previous conclusions. Leaves from the albino bough and from a contiguous green bough, collected on August 17th, 1880, gave the following results:—

	White.	Green.
Water	72.69	58.08
Organic matter	24.65	40.33
Ashes	2.66	1.59
„ from leaves dried at 100°	9.73	3.79
K_2O { in ashes from dried }	51.28	25.62
P_2O_5 { leaves }	14.64	17.05

The ashes from a larger quantity of leaves collected on July 30th, 1886, were analysed with the following results:—

	White.	Green.
Ashes from dried leaves	8.33	3.85
100 parts ashes contained:—		
K_2O	49.38	29.10
CaO	8.25	24.50
MgO	6.52	9.55
Fe_2O_3	0.82	1.24
Mn_3O_4	2.08	2.36
P_2O_5	14.25	15.80
SO_3	7.18	10.05
Cl	4.25	1.25
SiO_2	3.15	4.25
	95.88	98.10
Deduct oxygen for chlorine ..	0.96	0.32
	94.92	97.78
CO_2 , Na_2O , &c., by difference..	5.08	2.22
Total nitrogen	3.94	2.78
Albumenoid nitrogen	2.65	2.41
Non-albumenoid nitrogen ..	1.29	0.37

The respiration and transpiration of the two kinds of leaves were also studied.

DISCUSSION.

Mr. WARINGTON said that the key to the difference in composition between the white and green leaves lies apparently in the fact that the former do not assimilate carbon but live practically a parasitic life. The same root-sap being primarily supplied to both kinds of leaves, the white must be richer in sap-constituents, as they contain a larger proportion of water. This fact, however, only partly explains the great preponderance of potash and other sap-constituents in the white leaves. We must

further recollect that the sap of the green leaves has done far more work than the sap of the white leaves, its active constituents have indeed been consumed for the formation of tissue. The green leaves contain far more organic matter than the white; but this corresponds to only a small part of the work done. The green leaves have, in fact, furnished organic matter for the nourishment of the whole tree, and the organic substances transferred from the leaves to form woody tissue have doubtless been accompanied by the necessary sap-constituents. The sap of the green leaves is thus to a great extent exhausted sap. One constituent, however, preponderates in the green leaves, viz., lime. Salts of calcium occur largely as encrusting matter in old leaves; these salts have accumulated more in the green leaves, as a result of greater evaporation from the surface, and probably, from the removal of the carbon dioxide which held them in solution. In the white leaves there has been less evaporation, and a production instead of removal of carbon dioxide.

95. "The Synthetical Formation of Closed Carbon-chains. Part II. Some Derivatives of Tetramethylene." By W. H. PERKIN, Jun., Ph. D.

In a previous paper (*Trans.*, 1885, 801) the author has shown that if the sodium compound of ethylic malonate be treated with ethylenebromide, ethylic trimethylenedicarboxylate (1, 1), $\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix} \text{C}(\text{CO}_2\text{Et})_2$, is formed. The action of trimethylene bromide on ethylic sodiomalonate has now been studied, and the derivatives of tetramethylene thus obtained are described in the paper.

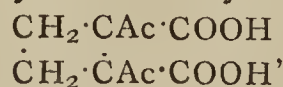
The first product of the reaction is ethylic tetramethylenedicarboxylate, $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \dot{\text{C}}(\text{COEt})_2 \end{matrix}$, which is a colourless oil, boiling at 223°. On hydrolysis this salt is converted into tetramethylenedicarboxylic acid (1, 1) (m. p. 154—156°), which in its turn is easily converted on heating into tetramethylenecarboxylic acid, $\text{C}_4\text{H}_7 \cdot \text{COOH}$ (b. p. 191°), and carbonic anhydride.

A second method of synthesising tetramethylene-derivatives is the following:—

The product of the action of one molecular proportion of ethylenebromide and two molecular proportions of ethylic malonate is ethylic butane- $\omega_2\omega_2$ -tetracarboxylate, $(\text{CO}_2\text{Et})_2\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$. When this salt is treated with sodium it forms a disodium-derivative, which by the action of bromine is easily converted into ethylic tetramethylenetetracarboxylate (1, 1, 2, 2), $\begin{matrix} \text{CH}_2 \cdot \text{C}(\text{COOEt})_2 \\ \text{CH}_2 \cdot \dot{\text{C}}(\text{COOEt})_2 \end{matrix}$.

Tetramethylenetetracarboxylic acid is a colourless crystalline mass, melting at 145—150°. On heating it is easily converted into tetramethylenedicarboxylic acid (1, 2) (m. p. 130°) and carbonic anhydride. The anhydride of this latter acid (m. p. 76—78°) is obtained by heating the acid to 300°.

Diacetyltetramethylenedicarboxylic acid,



is obtained in a similar way from the product of the action of one molecular proportion of ethylene bromide and two molecular proportions of ethylic acetoacetate. It is a colourless crystalline mass melting at 210°.

96. "The Action of the Halogens on the Salts of Organic Bases. Part II. Tetramethylammonium Salts." By LEONARD DOBBIN, Ph.D., and ORME MASSON, M.A., D.Sc., Chemical Laboratory of the University of Edinburgh.

The actions of the halogens on the tetramethylammonium salts pretty closely resemble those on the trimethylsulphine salts described in a previous paper.

Of the addition products obtained from haloid tetramethylammonium salts, those which contain one atom of

iodine are brightly coloured crystalline compounds of considerable stability. The crystals of the dibromiodide, Me_4NIBr_2 , are orange, and those of the dichloriodide, Me_4NICl_2 , are yellow. Both of these substances, like the corresponding trimethylsulphine-derivatives, take up ammonia gas, the dichloriodide doing so more readily than the bibromiodide.

A chlorobromiodide was not obtained by acting on tetramethylammonium bromide with iodine monochloride, but a dichloriodide was formed, the bromine being displaced by chlorine. In this respect the tetramethylammonium series differs from the trimethylsulphine series.

Those addition products which contain only bromine or chlorine, or both, are very unstable substances, and rapidly lose halogen in air, leaving haloid salts. Some of these were obtained in crystals but not in a pure state, being always mixed with some haloid salt.

An experiment in which tetrethylphosphonium iodide was acted on by bromine proved that the reaction took place in the case of the phosphorus bases also, a crystalline product being obtained.

97. "Glycyphyllin, the Sweet Principle of *Smilax glycyphylla*." By EDWARD H. RENNIE, M.A. (Sydney), D.Sc. (London), Professor of Chemistry in the University of Adelaide, South Australia.

Smilax glycyphylla is a plant which grows in abundance on the shores of Port Jackson, and is common on the coasts of the northern parts of New South Wales and the southern parts of Queensland; the sweet principle extracted from its leaves has already been partially examined by Dr. Wright and the author (*Trans.*, 1881, 237). The author now corrects the formula previously given to $\text{C}_{21}\text{H}_{24}\text{O}_9$; glycyphyllin separates from aqueous ether with three, and from water with four and a half molecules of water of crystallisation. On hydrolysis, it yields phloretin and isodulcite:

$\text{C}_{21}\text{H}_{24}\text{O}_9 + 2\text{H}_2\text{O} = \text{C}_{15}\text{H}_{14}\text{O}_5 + \text{C}_6\text{H}_{14}\text{O}_6$,
and is therefore closely allied to phlorizin, with which it is proposed to carefully compare it.

PHYSICAL SOCIETY.

November 13th, 1886.

Prof. BALFOUR STEWART, President, in the Chair.

IN opening the proceedings the PRESIDENT referred to the great loss which the Society had recently sustained by the death of Prof. Guthrie, F.R.S., the founder of the Society and his predecessor in the chair. In the capacity of Demonstrator Prof. Guthrie contributed materially to the success of the Society's meetings, and his decease is deeply regretted.

The PRESIDENT also announced that the Council were considering what steps should be taken to commemorate the late Dr. Guthrie, and that a circular expressing their views would be placed before the members in a few days.

The following papers were then read:—

On the Peculiar Sunrise Shadows of Adam's Peak in Ceylon. By the Hon. RALPH ABERCROMBY, F.R. Met. Soc.

The author prefaced his description by an extract from a paper on the same subject, by the Rev. R. Abbay, read before the Society May 27th, 1876, in which the explanation proposed is that the effects are caused by total internal reflection, as in ordinary mirage, the difference of air density being in this case due to the low temperature at high altitudes. The author pointed out that Mr. Abbay neglects the difference of density due to elevation, and that his own thermometric observations disprove conclusively any idea of mirage. The chief phenomena observed were, 1st, the appearance of a circular rainbow with spectral figures near the top of the shadow of the peak; and 2nd, a peculiar rising of the bow and shadow, which seem to stand up in front of the observers. Both

these effects are traced to the existence of mist clouds in the vicinity of the shadow. Two dark rays or brushes were seen to shoot outwards and upwards from the circumference of the bow, in directions nearly coinciding with the prolongations of the edges of the shadow, when seen projected on the lower mist clouds; but the author does not attempt to explain this phenomenon. On one occasion a second and outer bow was seen. The times during which the phenomena were visible were too short to permit sextant observations being taken, but the diameter of the inner bow was estimated at 8° or 12° . A totally distinct kind of shadow is sometimes seen from Adam's Peak just before and at the moment of sunrise, which seems to stand up against the distant sky. The author found, at Pike's Peak, Colorado, a similar effect, which is visible only at sunset.

Mr. G. GRIFFITHS remarked that he had often seen similar appearances to those described, in Switzerland.

In answer to questions by the President and Prof. S. P. Thompson, the author said the reason why the shadows were seen at Adam's Peak at sunrise and at Pike's Peak at sunset was that the configuration of the land on the west side of the former was similar to that on the east sides of the latter, both being low, whereas the opposite side were high, and therefore unsuitable for showing the phenomena. In all cases he believed the appearances due to the shadows being projected on clouds of suspended matter in the air at various altitudes. He had not noticed whether the colours were reversed in the second bow seen from Adam's Peak, but observed that this bow nearly, but not quite, touched the inner one.

"Note on the Internal Capacity of Thermometers." By A. W. CLAYDEN, M.A., read by Prof. REINOLD, Secretary.

The author proposes to determine the volume v of the mercury by measuring the capacity c of a detached piece of the same tube of known length, and thence inferring the volume of t degrees of the thermometer, the length of which is equal to the length of the tube taken. By assuming the value of a (the coefficient of apparent expansion of mercury in the particular kind of glass) to be known, the volume of the mercury in the thermometer can be calculated since $c = t a v$.

Prof. RÜCKER remarked that there were often considerable differences in the sectional area of different parts of the same tube, and hence the method would probably not be very reliable.

On the motion of the PRESIDENT, a vote of condolence to Mrs. Guthrie on her sad bereavement was passed unanimously.

OBITUARY.

ROBERT ALEXANDER.

THE earthquake of August 31st, 1886, which spread consternation through so large a section of the United States, was especially disastrous in Charleston, S.C., in which city were many fatal casualties. Among the victims of this terrifying catastrophe was a young English chemist, Robert Alexander.

Mr. Alexander was born on the 18th day of March, 1863, at Tranmere, near Birkenhead, Cheshire. His father, William, and his mother, Margaret McLean Adam, were natives of Scotland, but removed to London about 1874, and young Alexander received his early education in the schools of the metropolis. While at school he developed a taste for chemistry, and while yet quite young made considerable progress in his favourite study.

After leaving school he was apprenticed to G. W. Wigner, F.I.C., F.C.S., the well-known analytical chemist. Here he became a skilled analyst, and soon obtained a position as Manager in the Fish Phosphate Works, on the

Thames, some distance from London. He remained there about two years, but, desirous of seeking a larger sphere for his activity, he was induced to go to the United States, where his maternal uncle resides, and where he arrived in January, 1886. In the March succeeding he went to Charleston, S.C., the head-quarters of the fertiliser industry, and had only just taken hold of a sanitary system in that city when death came on the fatal night of August 31st. He was killed instantly in trying to escape to the street, being struck by falling bricks. His remains were interred in Magnolia Cemetery on September 1st. One who knew Mr. Alexander well says of him—"He had taken a wide survey of the domain of physical science; he was a careful, painstaking, and accomplished analyst, conscientious and thorough; while his beautiful simplicity and his noble Christian virtues not only endeared him to all who came in contact with him, but demanded that meed of recognition which such a character alone is worthy to receive."

NOTICES OF BOOKS.

Eighty-fourth Annual Report of the Chief Engineer of the Philadelphia Water Department for the Year 1885.
Philadelphia: Dunlap and Clarke.

WERE we cynically disposed we might find in this Report no little scope for self-congratulation. Sanitary reform is difficult enough on this side of the Atlantic, and difficulties not a few are thrown in its way. But we have not yet heard of a municipality formally endeavouring to restrain one of its officials from lecturing on the perils of drinking polluted water. All persons who take an interest in the water-supply of cities will find in this volume not a few most instructive facts.

We learn that certain large consumers of water, such as brewers, contrived to pay "about 50 per cent only of their actual dues to the City."

In another class of cases "certain persons having 'influence' of some sort seemed to have acquired a certain exemption from payment of water-rents altogether, and were shown to be delinquent for several years together."

Only about one-quarter of the dwellings in Philadelphia are closetted, though about one-half have baths. There are 7357 dwellings and 13,623 "half dwellings" not supplied with water at all.

The introduction of water-meters has effected a saving in the water consumption, which, in some instances, runs up to 70 per cent. Prior to the introduction of the meter "a pipe would be used to fill a tub, and the workman would throw the hose upon the floor and let the water run until he had again occasion to use it. In other cases a pipe in constant flow during the day would also be allowed to run after shutting down the mill. Leaking pipes were not repaired, nor were urinals and basins shut off." Such facts show that companies and municipalities would not necessarily be losers by adopting the meter instead of the inequitable system of payment by rateage.

It appears that 80 per cent of the Philadelphia water-supply is taken from the Fairmount Pool, which "is used in effect as a general cesspool for the riddance of the foulest and most deleterious waste matters, . . . the city itself permitting and participating in this violation of law and decency." Laws passed as far back as 1824, 1828, and 1832 did indeed forbid, under appropriate penalties, the throwing or depositing in that part of the River Schuylkill which is between the dam at Fleet Rock and the dam at Fairmount "any carrion or carcass, any excrement or filth, any offal or noxious matter, or any matter or liquid from any dye-house or manufactory, calculated to render the water of the said river impure." These judicious laws remained dead letters, and when, in 1868, it was sought to revive them, the manufacturing interest

had the effrontery to unite in an effort to prevent it, and their action unfortunately proved successful. They pleaded for the retention of the river as a sewer, and protested against an intercepting culvert. How little the citizens of Philadelphia are disposed to obey and support sanitary regulations, and with what impunity such laws can be set at defiance, appears from several cases which space does not permit us to quote.

From an order written by the Clerk to the Board of Health it appears that there are at least 50,000 cess-pools (!) in the city, which, together with miles of leaking sewers and numerous graveyards, are constantly discharging foul matter into the bed of water underlying the city. Hence it appears that Philadelphia is, or at least was, still suffering from the nuisance of intramural interment. However, cremation is making good progress in the United States, so that we may hope this source of danger will soon be at an end.

Some experiments on the aëration of the water-supply of one district of the city are of profound interest. Comparative analysis showed a reduction of the free ammonia by 76 per cent, and of the albumenoid ammonia by 40 per cent, whilst the total solids are diminished and the nitrous acid eliminated altogether.

The reports of Profs. Mallet, Wormley, and Greene, and that of Dr. Leeds, clearly show the progressive pollution of the river, and point out the danger which will be incurred if once the bacillus of cholera is introduced into the water. These gentlemen, and indeed the Chief Engineer himself, show such a complete grasp of the subject, and expound the water question so clearly and fully, that the Philadelphians, if they still tolerate the use of polluted water, will be emphatically "sinning against better light and knowledge."

Report on the Chemical Examination of the Waters of the Public Wells of Albany, New York. By WILLIS G. TUCKER, Ph.D. Albany: Burdick and Taylor.

THE author, in the general description of the wells, prefixed to his analytical results comments very judiciously upon shallow wells in cities and populous districts as liable to sewage pollution. Even deep wells, he argues, in such localities can scarcely be preserved from animal contamination. In proof of the powerlessness of filtration to remove specific disease germs, he describes the decisive case which occurred at Lausen in 1872. But that typhoid fever and cholera "are seldom communicated in any other way" is scarcely a safe conclusion.

Dr. Tucker admits that a water, apparently chemically pure, may contain enough morbid matter to convey disease. For all this he holds that chemical analysis is of value in determining the sanitary rank of a water, since the more animal pollution can be traced the greater is the probability of morbid matter being sometimes introduced. He emphasizes the caution that the sensible properties of a water throw little light upon its real quality. It is satisfactory to learn that urban wells are being extensively closed in the United States. The analytical process employed is that of Wanklyn and Chapman. Of the thirty-six wells sampled he condemns fifteen as bad and thirteen as doubtful, while five are described as fair and three as good. The two former groups he recommends to be closed, whilst the two latter should be subjected to occasional re-examination.

CORRESPONDENCE.

RADICAL v. RADICLE.

To the Editor of the Chemical News.

SIR,—Mr. Madan's invitation, some months ago, to those chemists who refuse to replace the term *radical* by *radicle*, to defend their action, was accepted by me in your columns

(CHEMICAL NEWS, liv., 36), after I had waited a time to see whether others would not do so. He replied to me (CHEMICAL NEWS, liv., 71), and must be supposed to have placed before your readers all the grounds on which English chemists are being persuaded—I might say coerced—into making this replacement in their writings. An examination of Mr. Madan's letters seems to show that there is nothing at all to be said in defence of *radicle* against the objections I have raised to its use in place of *radical*; and that the only reasons for condemning the use of the latter term are that it is an erroneous Gallicism, and not a substantive but an adjective.

As to the argument for the rejection of *radical* on the score of its not being a substantive, that was met, in my first letter, by pointing out how many adjectives there are in *-al*, which are also used as substantives. I need, therefore, only address myself now to the task of upsetting the other argument, that *radical* must be rejected as being an erroneous Gallicism.

From a Ciceronian Latinist's point of view *radical* may, indeed, be fitly called a Gallicism, and *radicalis* be condemned when found in a Latin theme. But from the same point of view the French language itself, with all its perfections, may be described as being, for the most part, a *corrupted form of Latin*! and, indeed, is so described by grammarians, without thought of casting any slight upon it. Were Mr. Madan only to consider to what a pass English would be brought, were all the *corrupted form of Latin*, which, as French, has come into it since the Conquest, to be cast out, he would probably hesitate before condemning the use of such a long-established and serviceable word as *radical*, merely because it is a Gallicism. But he says, further, of it, that it is an *erroneous* Gallicism. It is difficult to see in what consists this erroneousness. *Radicalis* is not found in a classical author, but it is just this fact which makes the use of *radical* a Gallicism. Linguistically, *radicalis* is an unimpeachable formation, and the actual Latin word *radicaliter* pre-supposes it. It should be remembered that this word *radical*, treated with such contumely by Mr. Madan, is to be found in Provençal, and, for hundreds of years since to the present time, has been in use in French (and Italian) as a philosophical and scientific term, occurring in all departments of literary thought, and not as an adjective merely, but as a substantive. From French it has passed into German and English, and has become, perhaps, the commonest of philosophical terms in the literature of chemistry. Strange, since there was all along at hand the classical word *radicula* (L.), *radicule* (F.), *radicle* (E.), that this term should have been so long passed over in favour of *radical*, if it really has the needed signification, *radical*—the term adopted—being all the while but an erroneous Gallicism! *Radicle*, as I pointed out in my first letter, is certainly not capable of taking the place occupied so long by *radical*. Beyond a special technical use in botany, it has never crept into science till now in chemistry, never at all been used as an abstract term, but always with the force of a diminutive; whereas, be it rightly or wrongly formed, *radical* has ever been indisputably the adjective form of *radix* or root, with no sense of diminutiveness attached to it.

It is a gratification to me to see Mr. John Spiller so entirely with me in opinion (CHEMICAL NEWS, liv., 83); I was not aware till now, that he had so many years ago appeared in the CHEMICAL NEWS as an opponent to the substitution of *radicle* for *radical*. Concerning his reference to the paper in the *Journal of the Chemical Society* by Mr. Shimidzu and myself, upon *Mercury Sulphites*, it is as he supposes: the word *radicle* was not in our manuscript.

I would urge upon Mr. Spiller, and others agreeing with him and myself, to make a firm protest to the Publication Committee of the Chemical Society against their effort to enforce the use of *radicle* being longer continued, on the grounds that the recognition they are giving to this word is derogatory to the literary reputation of English chemists,

and an uncalled for manifestation of British insularity. Mr. Spiller and those with him, as well as myself, in advising this course, could not be accused of presumption in making this protest, since they would only be deprecating the action of the Committee in repudiating, as unscholarly, the practice, not only of a past generation of English chemists and of many of the present time, but of the entire body of chemists, past and present, of France, Germany, and, indeed, all Europe.—I am, &c.,

EDWARD DIVERS.

The Imperial University of Japan,
October 1, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 18, November 2, 1886.

Atomic Weight of Gadolinium Oxide.—A. E. Nordenskiöld.—(See p. 241).

Saturation of Selenious Acid by Bases and Acidimetric Determination of this Acid.—Ch. Blarez.—The reactions obtained with baryta water are distinct and precise, and may serve for the acidimetric determination of selenious acid. There is added to the acid liquid a drop of helianthine and a drop of phenolphthalein. The liquid becomes rose-coloured. When the baryta water has been added until half the molecule is saturated the liquid loses completely every trace of rose, and becomes yellow. The yellow remains until the molecule is entirely saturated, when it gives place to a new rose colouration.

Synthesis of Pentamethylene-diamine, Tetramethylene-diamine, Piperidine, and Pyrrolidine.—A. Ladenburg.—This paper does not admit of useful abstraction.

Two Novel Chloro-Derivatives of Methyl-benzoyl.—H. Gautier.—The compounds in question are trichloromethyl-benzoyl, and the corresponding bichloro-compound. The study of these two compounds shows how great is the stability of the chlorine which they contain in proximity to carbonyl, since, under the influence of the sparingly energetic reagents which easily attack the chlorine of the chloro-aromatic carbides contained in the chains, they are attacked only slowly. As for the more energetic reagents, their action bears upon the acetonc grouping, and we thus fall back upon a mono-substituted derivative simpler than benzol.

Novel Reaction of Aluminium Chloride; Syntheses in the Fatty Series.—Alph. Combes.—In studying the action of this reagent on a class of bodies containing oxygen and chlorine, the acid chlorides and the chlorinised aldehyds, the author has found a reaction which has enabled him to effect some syntheses. He has, in the first place, studied its action upon acetyl chloride, and has obtained a compound, $C_{12}H_{14}O_6Al_2Cl_8$. This compound is permanent in dry air, but it is at once decomposed by water.

Hæmatoscopy, a Novel Method for the Analysis of Blood, based upon the Use of the Spectroscope.—M. Hénocque.—This paper requires the three accompanying figures.

Bulletin de la Société Chimique de Paris.
Vol. xlv., No. 4, August 20, 1886.

Transformation of Glucoses into Dextrines.—E. Grimaux and L. Lefèvre.—Already noticed.

Acidimetric Determination of Sulphurous Acid and of Sulphites.—Ch. Blarez.—The author refers to

his communication to the Academy of Sciences (June 5, 1886), and adds that the volumetric determination of sulphurous acid is not only practicable when it exists alone in an aqueous solution, but also when it is mixed with other acids, mono- or poly-basic, if so strong that their absolute basicity can be detected by cochineal or helianthine. In this case we make two successive determinations, the one in presence of cochineal and the other in presence of phenolphthalein. The difference expressed in c.c. of normal alkali multiplied by 0.064 gm. represents the weight of anhydrous sulphurous acid contained in the quantity of liquid operated upon.

Heat of the Alloys of Lead and Tin.—W. Spring.—Liquid alloys behave like simple mechanical mixtures. If it is true that, all other conditions being equal, bodies are so much the more fusible as their molecules contain a smaller number of atoms, we conceive that an alloy should have a melting-point lower than the melting-points of its constituents.

Combination of Water with Salts.—E. J. Maumené.—The author finds that potash alum contains 49.83 per cent of water, which answers not to 24, but to 28.73 of water.

Crystalline Barium and Strontium Titanates.—L. Bourgeois.—The author has obtained these compounds by melting their elements in an excess of the corresponding chloride. Both these salts are titanates. Calcium yields also a titanate identical with Perowskite.

The Constitution of the Nitro-combinations of the Fatty Series.—P. Alexeyeff.—The author holds that nitro-ethane should be regarded as an isonitroso-ethyl alcohol.

Action of Heat on the Acetones.—P. Barbier and L. Roux.—The authors have studied the action of heat on dimethyl-carbonyl, benzophenon, and acetophenon. They find that the action of a red heat effects the separation of the carbonyl group in nature, which seems to justify the mode of notation adopted to represent the structure of these bodies. The hydrocarbon groups, when set free, either unite simply among themselves or undergo separately the action of the red heat, giving rise to their ordinary products of condensation and hydrogenation.

On Bromo-Substitutions in the Aromatic Series.—E. Werner.—This paper does not admit of useful abstraction.

Preliminary Note on Aluminium and Glucinium Silico-fluorides.—C. Chabrière.—The author has verified the statements of Berzelius and of Attenberg on their compounds, but he indicates methods by which both can be obtained not in a mass, but in well-defined crystals.

On Hydrated Copper Sulphates.—H. Lascœur.—The crystalline hydrate gives off the water which it contains—even water of interposition—with great difficulty, and re-absorbs it in the same manner, a phenomenon which seems to be connected with the hardness of the crystals. When finely powdered this salt is more easily dissociated, a property which seems connected with the greater surface which it presents. If exposed on a hot plate the product is dehydrated in a most irregular manner, constituting a mass far from homogeneous,—a property connected probably with its bad conduction of heat.

Reactions produced by Metallic Salts in the Aqueous Solution of Dipropylamine.—Camille Vincent.—The salts of magnesium, glucinium, aluminium, zirconium, manganese, zinc, cadmium, tin, antimony, bismuth, and lead give white precipitates; ferrous salts give a greenish, and ferric salts an ochrey precipitate; the salts of chrome form green, those of cobalt blue; nickel apple-green, uranium yellow precipitates. Mercurous salts give a black, and mercurous salts a yellowish; silver a grey; palladium a buff gold or light yellow, turned to a deep violet by excess. Platinum gives no precipitate.

MISCELLANEOUS.

Treatment of Patent Affairs.—By Dr. G. Krause, of Cöthen.—We have often observed that documents intended for the Patent Office, *e.g.*, applications for patents, are not worked out with that care and knowledge which the importance of the subject unquestionably necessitates. Hence there arise for the inventor difficulties and expenditure which are not unimportant, and which might have been avoided if he had not rested in the belief that the documents drawn up by a professional expert must always bear the stamp of practical knowledge and conscientiousness. Above all things there is here delay in the course of the affair, and there is even the possibility of protection being refused in consequence of inaccurate or ambiguous specifications. Applications are sometimes made to us to know how such patent applications are to be re-cast, so that they may comply with the requirements of the Patent-Office. It will be manifest to any one who has been engaged in such affairs that such re-modellings are far more difficult and tedious than new commencements, and that in many cases the specification cannot be drawn up in the meaning of the original application. It is, therefore, absolutely necessary that the inventor should submit the documents, which are handed in to the Patent Office, in his name to a proper revision. In proof we will give a few examples with which we have recently come into contact. We were entrusted by an Austrian firm with a patent-application for Germany, and there was sent to us, by way of basis, the application which had been given in in Austria. This application, which referred to a new sizing for paper, was so superficial, and had been drawn up with so little knowledge of the matter, that it required a complete re-modelling in order to make the subject of the invention intelligible. Thus, mention was made throughout of sulphates, instead of sulphites, though the former did not come into play at all. Instead of "dissolved sulphites" there was mention of "disturbed sulphites," "abietinic salt" instead of abietinic salt, &c. In a word, the specification betrayed absolute ignorance of the very elements of chemistry. In another case a liquid was to enter a space and be converted into a vapour by collision with a solid surface, and was then, further, to undergo a chemical change by the introduction of a certain agent. The inventor, himself a chemist, had given a perfectly clear description of his process. But the expert had caused the liquid to enter the space as a vapour, and to undergo the subsequent transformation by contact with the solid surface. The final product was separated out as a "colourless powder." In spite of the false description the patent was granted, but it is substantially worthless, as it protects a process which the inventor does not use, whilst his real process is unprotected! Applications for patents are often full, not merely of technical defects, but even of orthographical errors. The author finally cautions inventors to take the greatest care in the description of their processes, and to place them in the hands of trustworthy patent agents. (In England the patent agent consults with his client both on the preliminary and the final specification before filing, or, if this is not possible on account of absence, a draft of the document is forwarded to the inventor for his approval. Still both technical errors and ambiguous language not unfrequently occur in specifications).

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Combustion Furnace.—Does any reader use the Glaser Combustion Furnace, and is it as satisfactory in working as Hoffman's?—
EBLANA

MEETINGS FOR THE WEEK.

SATURDAY, 27th.—Physical, 3. "Note on a Method of Measuring the Coefficient of Mutual Induction of Two Coils," by Prof. G. Cary Foster, F.R.S. "On the Stability of Liquid Films," by Prof. A. W. Rücker, F.R.S.

TO MANUFACTURING CHEMISTS AND OTHERS,
THE METROPOLITAN BOARD OF WORKS will meet at the Office of the Board, Spring Gardens, S.W., on FRIDAY, the 3rd day of December, 1886, at Twelve o'clock at noon precisely, and will then be prepared to OPEN TENDERS by parties who may be willing to contract for the supply of 200 tons of Protosulphate of Iron (Commercial Green Vitriol) to the Main Drainage Pumping Station at Crossness, near Belvedere, Kent. Parties desirous to submit Tenders may obtain a copy of the Specification and Form of Tender, on application to the Chemist of the Board, at the Office, Spring Gardens, between the hours of Nine a.m. and Four p.m. (or on Saturdays between the hours of Nine a.m. and Two p.m.), until Thursday, the 2nd day of December, 1886). The Tenders, which must be on the form supplied from this Office, and addressed to the Clerk of the Board, are to be delivered at the Office before Four o'clock on the last-mentioned day, and no Tender will be received after that hour. The Parties tendering must be in attendance at the Board at Twelve o'clock on the day appointed for opening Tenders, and any Tender which is not fully filled up in every particular will be rejected.

The Board do not bind themselves to accept the lowest or any Tender.

Spring Gardens, S.W., 18th November, 1886.

J. E. WAKEFIELD, Clerk of the Board.

The BADISCHE ANILIN und SODA FABRIK of STUTTGART and LUDWIGSHAFEN-ON-RHINE hereby give Notice that Legal Proceedings will be taken against all Persons making, selling, or using any AURAMINE (patented March 26th, 1884, No. 5512) not manufactured by the Company or their Licensees, *The Society of Chemical Industry of Basle*.

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THE CHEMICAL NEWS.

VOL. LIV. No. 1409.

ON THE FADING OF WATER-COLOURS.*

By W. N. HARTLEY, F.R.S.,

Professor of Chemistry, Royal College of Science, Dublin.

UNDER the title "Light and Water-colours" an article has been published in the *Nineteenth Century* (page 849, No. 112, June, 1886), in which reference is made by the author, Mr. J. C. Robinson, to a correspondence conducted by various writers in the *Times* newspaper. This correspondence, which I have not had an opportunity of reading, appears to have consisted in no small measure of opinions and assertions incompatible with the observations of the author. It has been asserted by eminent authorities that water-colour drawings not only do not fade, but that they actually "deepen in tone" by age; but even those who assert that drawings do not fade, nevertheless admit that direct sunlight is detrimental in some way to water-colours.

Mr. Robinson maintains that water-colours are seriously injured by direct sunlight in a comparatively short time, and deteriorate by exposure to diffuse daylight to such an extent that he quotes the suggestion of Mr. Ruskin, made some years ago with reference to Turner's drawings, that they should be kept either in portfolios or—if framed and glazed—in cabinets from which light is excluded.

Considering the inestimable value of the works of Girtin, John Varley, De Wint, Copley Fielding, Turner, and David Cox, every lover of pictures will appreciate the importance of any definite information on the subject of the action of light on colours, inasmuch as it will afford a means of arriving at a decision on this question.

Works in water-colours are painted with pigments of two distinct kinds, namely:—

- (1.) Mineral substances: for the most part these are—
 - Metallic oxides.
 - „ sulphides.
 - „ silicates.
- (2.) Organic substances:—
 - Stable colouring-matters.
 - Unstable and changeable colours.

With the exception of ultramarine and colours containing lead or mercury, the bodies of the first class may generally be considered as unalterable; those of the second class may be considered as alterable *under certain conditions*.

It has been shown by the researches of Chastaing—"Etude sur la Part de la Lumière dans les Actions Chimiques" (*Annales de Chimie et Physique*, Series 5, vol. xi., p. 145)—that the chemical action of light upon mineral substances promotes oxidation by means of the red rays of the spectrum, the oxidising power, however, diminishes as the rays are more and more yellow in colour; the green rays are without action, and form a neutral region; but the blue rays reverse the action of the red, for they promote the reduction of compounds to the metallic state, and this reducing action increases in power as the rays of the spectrum decrease in wavelength, being at the maximum in the extreme violet region. With organic substances the chemical action of light is quite different; it promotes an oxidising action throughout, commencing in darkness; it continuously increases in power as the rays extend through the red and yellow into the violet end of the spectrum. There is, however, a modification in the green; the oxidising power then

falls off, but the mean effect of light on organic bodies varies in strength according to the following figures: if represented in darkness by 1, in the red is about 2, in the violet 3 to 4. The violet rays are twice as strong in promoting oxidation as the red. It must not, however, be assumed that sunlight has no other chemical action than that of promoting oxidation or reduction; if this were so, then the preservation of colours could be secured by protecting them from air and moisture.

The colour of an organic substance is an evidence of its highly complex structure, notwithstanding the fact that its composition may be simple enough. It may consist, for instance, of but three elementary substances, carbon, hydrogen, and oxygen,—or of four, carbon, hydrogen, oxygen, and nitrogen,—but the number of atoms of these substances necessary to produce the smallest particle or molecule of colour is large, and every colour depends upon the way in which the atoms are arranged in the molecule. The shifting of a single atom will cause a brilliant colour to become colourless. Now the effect of light on such substances is variable; sometimes the change induced is oxidation, and this is the case with the bleaching of turmeric; but it is also sometimes a molecular change, or the re-arrangement of the atoms in the molecule,—and such undoubtedly is the change discovered by Pasteur, by which the substance quinine, under the influence of light alone, becomes converted into a distinctly different body (quinicine) without its actual composition being altered.

We can also understand how light may be capable of resolving a complex substance into two or more simpler substances.

A pigment is a substance which intercepts or absorbs certain of the rays of which white light is composed, and permits the remaining rays to pass through it. Gamboge, for instance, absorbs the red, green, blue, and violet rays, and transmits the yellow. Visible rays of light are the effect of vibrations which are of least rapidity in the red and greatest in the violet. The ultimate particles or molecules of substances are in constant vibration, and the rapidity of the vibration of the molecules of a coloured substance is indicated by the rapidity of vibration of the rays which the coloured substance absorbs. In other words, the colour of a substance depends upon the rate of vibration of its molecules. The more brilliant the light the more ample are its vibrations. It is easy, then, to understand how a light of great brilliancy may throw a coloured molecule into such a state of intense vibration that the molecule falls to pieces. The complex and unstable compound is resolved into two or more simple and colourless bodies. Under these circumstances the absence of air or oxygen would have no retarding effect upon the bleaching action of light.

The reagents which may cause a change in unstable colours are oxygen, moisture, and acidity.

With regard to *oxygen* it may be said that, inasmuch as water-colours are never mounted in air-tight frames, they are always more or less subject to its action. This is, of course, especially the case if the framing of a picture is alternately heated and cooled by the sun shining upon the glass during a portion of the day, for, upon cooling, fresh air enters to take the place of that removed by expansion.

Moisture is not sufficiently protected against; moisture is used in the process of mounting drawings, and the subsequent drying is more or less imperfect according to the humidity of the atmosphere at the time. Air contains from about 0.5 to 1.5 per cent of water vapour, and the fibrous nature of paper is such that it always retains a certain amount of moisture, and although this may be very small, yet—considering the very minute quantity of colouring-matter in light and delicate washes which it may affect—it is necessary to take account of its presence. The boards at the back of a drawing, if of wood or of card, also contain moisture.

Acidity.—The air of towns where much coal is con-

* A Paper read before the British Association, Birmingham Meeting, Section B.

sumed, and where large manufacturing operations are carried on, is always acid, and the moisture of such air may be regarded as a mixture of very dilute sulphuric and sulphurous acid. The air of Manchester, for instance, in the centre of the town, may be perceived to be distinctly sulphurous in flavour, even in fine summer weather. This condition of the air is no doubt capable of causing serious injury to water-colour drawings. In a similar manner galleries which are lighted by gas, unless very efficiently ventilated so that the products of combustion are removed as fast as generated, are liable to receive upon their walls a deposit of dew which is acidified with sulphuric acid. This is well understood to be injurious in libraries. The sizing of paper may in time become acid if damp; the paper itself may be acid, for the fibre of which it is made is subjected to treatment with dilute acids, and the subsequent washing with pure water does not entirely remove the acid reaction from linen fibre. Many samples of the best drawing paper have recently been carefully tested, and the result has shown that it has always an acid reaction. This no doubt could in time act injuriously upon certain pigments, among which ultramarine may be particularly mentioned. This blue is very easily destroyed by the action of dilute acids. Size which has an acid reaction should never be used for drawing paper.

Having considered the acidity of the air and of the paper, it is necessary not to omit an examination of the colours. To the credit of the colour-makers be it said, that of sixteen tints commonly used in out-of-door sketching, only one, bistre, had a slightly acid reaction: the neutral character of the other preparations is decidedly in favour of their stability; furthermore, they are not likely to react on each other. Certain lakes which were known to the ancients, such as those prepared from the madder, are of remarkable stability, and so likewise in a greater degree are various preparations of indigo. It may be remarked that a particular blue colour found in the wall paintings decorating the baths of Titus was of organic origin, since Sir Humphry Davy proved it to be combustible. The only blue colour of an organic nature known to the ancients was indigo (*indicum purpurissimum*): there can be little doubt that this blue was indigo, and that it had withstood the action of air and sunlight for ages. In fact, neutral or alkaline indigo is a remarkably permanent pigment.

Chemists are familiar with the fact that *solutions* of indigo made with acids are converted, under the action of air and sunlight, into a brown substance. Hence it is obvious that acid preparations of indigo may undergo a similar change if washed over paper.

Gamboge in time is bleached by exposure to air and sunlight; this fact may be observed in many drawings which have been hung for the last fifty years.

In order to satisfy myself as to the alterability of colours I have made delicate washes of pigments on drawing paper of the first quality. The sheets of tinted paper were cut into two or three pieces; one was kept in the dark, one was exposed to the light, and a third was treated with hydrogen peroxide, and in some cases with a solution of sulphurous acid. It was considered as most probable that, in cases where the effect of sunlight is to promote the action of the oxygen of the air upon the organic colours, the result obtainable by air after a long exposure might be secured by the action of hydrogen peroxide with but little aid from the sun. The use of sulphurous acid was of course intended to show the probable effect of an atmosphere polluted by the combustion of much sulphurous coal or coal-gas. The colours tested were—

Blues.—Indigo, cobalt, ultramarine.

Yellows.—Gamboge, Indian yellow, cadmium orange, cadmium yellow, yellow ochre.

Reds.—Light red, Indian red, vermilion, crimson-lake.

Greens.—Viridian, olive-green, brown-pink, emerald-green.

Browns.—Brown madder, bistre, sepia.

Of these the following were affected by hydrogen per-

oxide:—Cadmium yellow and Indian yellow are bleached, olive-green is rendered slightly bluish in tint.

The following were affected by sulphurous acid:—Ultramarine, cadmium yellow, and Indian yellow. The first is bleached; the second nearly bleached, being converted into a very pale muddy yellow, and the same may be said of the third.

Vermilion has its brilliancy destroyed; it is rendered muddy and heavy-looking by sulphurous acid.

The other pigments were unaffected.

Considering now the action of sunlight, the blues were quite unchanged by exposure to air and sunlight for six hours a day for fourteen days.

Yellows.—Light washes of gamboge are completely bleached by exposure to pure air and intermittent sunshine for only three days, or in all eighteen hours; in a week's time even strong washes are much lightened in colour, and rendered dull if not bleached, while even three hours produce a very visible effect.

Reds.—Crimson-lake was the only one affected. Six hours' exposure to sunlight and air almost bleaches light washes, while three days, or eighteen to twenty-four hours with intermittent sunshine, cause even dark crimson to become very much lighter, and the purity of the colour is destroyed.

Greens.—Olive-green and brown-pink are rendered lighter in colour by six hours' exposure to sunlight and air. The olive-green becomes bluish and the brown-pink becomes brownish in hue and much lighter.

Browns.—Brown madder is slightly lighter after eight days, or forty-eight hours' exposure. Bistre fades with great rapidity; a light wash appeared much lighter after six hours. Sepia undergoes a change in colour which can scarcely be described as a tendency to bleaching; the tint becomes colder, but not very perceptibly lighter.

The action of sunlight, it will be noticed, differs from that of peroxide of hydrogen, and it may be regarded as probably not an oxidising action. To put this matter to the test and to ascertain whether a more permanent character might not be conferred on these unstable colours by protecting them from the action of air, the following tints were put upon paper in circular washes:—Crimson lake, gamboge, bistre, and olive green. Each disc was cut into three slips; one was kept in the dark, the second was exposed to light and air, and the third was enclosed between two plates of glass, the edges of which were kept together by gummed paper, which was made to enclose them completely and prevent the passage of air between the plates. The coloured discs were four inches in diameter. In the course of five hours it was found that the slips tinted with crimson lake and bistre and kept under glass were considerably altered, somewhat more so, it even appeared, than those which had been exposed to air; this was caused, however, by the very slight tint of the plate glass. It cannot be supposed that the air was absolutely excluded in this experiment, neither must the fact be overlooked that possibly there was sufficient air between the plates of glass to cause the colours to change; hence it is desirable that this experiment should be tried in modified form. The change in the colours was, however, progressive for several days, and hence it is extremely improbable that the colours were being oxidised. It is a proof, however, if proof be deemed necessary, that framed water-colours should, under no circumstances, be subjected to direct sunlight. Judging of the course of the chemical change, as observed to take place in lake and gamboge, it certainly appears as if the effect of sunlight on these colours was not one which induced oxidation, but rather a shaking asunder of the molecules into two or more colourless bodies.

It may be remarked that an impure atmosphere affects all preparations of lead; no preparation of this metal should be sold as a pigment, either for oil or water-colour painting. Some years ago Chinese white was made of white-lead, and in course of time it became brown; some shades of vermilion appear to be mixed with red-lead, and they

become dull or even blackish; Naples yellow of two shades fades, and is apt to become dirty in appearance subsequently. In short, the only preparation of either of the metals lead or mercury which should be used is pure cinnabar or vermilion, the sulphide of mercury. It is now obvious that mineral and organic colours, when used in combination, may be altered in this respect, that the mineral colours remain after those of an organic nature have been destroyed; or the more easily destructible of the organic colours may be destroyed, such as gamboge and crimson lake, and those of a more stable character, such as indigo, remain. With regard to the statement that water-colours do not fade there is this much truth, that many works of art, by ordinary exposure to diffused daylight in rooms and picture galleries, do not appreciably alter. It is also correct, according to my own observations, that some works, painted with colours which have been known to alter in certain cases, have been preserved, even though exposed to daylight for such a time as would lead to the expectation of seeing them changed.

There is little doubt that the surrounding conditions have made the difference. All the examples of the work of Girtin and John Varley which I have seen, and even some of the earlier pictures of De Wint and Copley Fielding, have suffered by some of the colours having faded. The trees have a sombre and unnatural blue tint, with here and there indications of brown, and the tone of colour is cold. The cause of this is doubtless due to the blue and the brown tints having remained, while the yellow has faded. It is probable that crimson lake has gone out of the foliage shadows. This change is, no doubt, one which may be described by saying that the work has "deepened in tone" by age, but the reason is that *the light of the picture has faded out of it*. The tints, therefore, are relatively darker, but not absolutely so. In some cases the blues may have suffered, but there is no appearance of this in any work that I can call to mind, with the exception of an alteration in the colour of clouds, which will be dealt with presently. There is one other cause for the "deepening of tone" in a water-colour drawing which must have been seen by everyone who has carefully examined a number of old drawings. The picture being on a white ground, the paper by age has become brown, as all paper does; the effect of this is of course a deepening of tone, in fact the effect is much the same as if the original were viewed through a glass tinted pale brown. One of the most valuable of pigments for clouds, distances, and shadows is ultramarine; with Indian red and light red it produces beautiful rich purple tones and cool greys, which exactly correspond with tints in the atmosphere. The value of these tints lies in the fact that they represent atmospheric effects seen when viewing distant mountains, the shadows of clouds, and other luminous shadows, and the reason is that the colour of the clear atmosphere is blue, and this is the medium through which other colours are seen. Whenever these tints have been mixed with ultramarine, as the blue pigment, the pictures are of a nature liable to suffer from the action of acids, and the atmosphere of a smoky town I should consider likely to be in the highest degree injurious to such works. The instance of dark purple or rich grey clouds becoming red, by the destruction of the blue pigment and the survival of the red with which it was mixed, is one which I have observed, and I am thus in agreement, so far, with Mr. J. C. Robinson's statement on the subject. He refers to the blue as being indigo, whereas that which was originally used in the works which have come under my observation was ultramarine, and my view is that it was destroyed by an acid and not by oxidation, or any such action induced by sunlight. If there are any well authenticated cases of indigo being destroyed when mixed with mineral reds there are also other instances of such a mixture being unaffected. Under these circumstances it would be well to consider the possibility of red pigments reacting on indigo. The fact has already been mentioned that

acid preparations of indigo are apt to be destroyed; if, therefore, the colour used was of this nature, we have a cause of its destruction. Even, however, if the indigo is of a neutral character the red pigment may be acid or may become acid.

Light red and Indian red are colours which may be made from calcothar, and calcothar of different shades is sold not only for the purpose of making colours, but in some work it is ground and sold as colour. Now calcothar is the residue of the material used in the distillation of Nordhausen oil of vitriol, and, owing to the incomplete decomposition of the ferric sulphate in the retorts, it not unfrequently is apt to contain a small quantity of basic ferric sulphate. This is not perfectly soluble at first, but on treatment with water it slowly yields an acid solution. These circumstances afford the conditions under which the indigo is most likely to become destroyed when mixed with such a red.

The result, on the whole, of these observations leads us first to devise a means of destroying the acid reaction of drawing paper, and so render it neutral or slightly alkaline. To this end it should receive a preliminary wash of a slightly alkaline solution. Caustic alkalies and alkaline carbonates are too strong, and apt to make the paper brownish, while the alkalinity of ammonia has not a sufficiently permanent effect upon paper. For the required purpose borax is to be preferred; it has been found to have no deleterious effect upon the colours, and in the case of bistre it increases its permanence. Of course the colours themselves should have no acid reaction; they should be properly tested for acidity before use, or at any rate, when this has not been done, borax may be dissolved in the water used for painting with. A pinch in half a tumbler of water is sufficient: thus any slight acidity in the pigments may be neutralised.

As to the preservation of drawings, works abounding in delicate golden tints representing sunlight effects, such as were painted by Turner, should be kept in apartments away from the influence of direct light from the sun, and generally in rooms with a very subdued illumination,—otherwise the yellows and crimson will certainly in time be destroyed, or at least will suffer. Work abounding in blue and grey tints, such as are seen in clouds, in distance, and the luminous shadows of rocks, should never be allowed to undergo the influence of an impure atmosphere; they should not be mounted on boards by means of adhesive material such as paste or glue placed at the back of them, and they should be kept perfectly dry. If they have already been so mounted, they ought to be carefully protected from the effects of damp.

Let us now consider what has been said with regard to the action of direct sunlight and diffused daylight. Mr. Robinson in his article says—"It must be obvious, inasmuch as the sun's light is the same, whether direct or infinitely lowered or mitigated, that it must in the exact measure of its intensity possess precisely the same properties." This sentence requires some little modification. The most intense rays of the sun as regards visibility are the yellow, but they promote in general very little chemical action, while the violet, which are the least visible, are those rays which promote chemical action much more strongly, probably two to three times as strongly as the yellow at least; while the ultra-violet rays, which are quite invisible under ordinary circumstances, are even more powerful than the violet. Moreover, those rays alone capable of chemical action on a coloured body are those more or less refrangible rays which the coloured body absorbs, and hence violet light would prove most destructive to yellow tints.

Then, again, the difference in intensity between direct sunlight and diffused daylight sufficient for the exhibition of pictures is so great that probably no one who has not measured the difference can appreciate its magnitude. It may be safely set down as generally forty times as great, and probably four hundred times as great in summer. According to this estimate a picture which would fade in

ten years in direct sunlight, might with care be exhibited for four hundred years, and probably for eight or twelve hundred years, if the yellow rays alone were used, or if the violet and the blue rays were diminished in quantity by the passage of light through blinds of unbleached linen (brown holland). It will be necessary to make exact experiments to dispose of all doubt concerning this point.

As far as lighting by electricity is likely to affect pictures the difference in intensity of action between the yellow and the violet, and those rays which lie beyond the violet, is a reason for a decided preference for incandescence lamps; the rays of the arc light are not only much more intense throughout the spectrum, but exceedingly rich in the violet and ultra-violet region, and therefore capable of very intense chemical action. The use of arc lights in a gallery of water-colour drawings must be considered as an unsafe mode of illumination, the adoption of which cannot be recommended.

In conclusion, it is obvious that those who desire to preserve valuable water-colour drawings should see that they are kept in a dry, pure atmosphere, and away from the influence of direct sunlight. Diffused daylight, when the drawings are not being exhibited, should be reduced by blinds of unbleached linen, which transmits a yellow or brownish light.

It is better in every case that water-colour drawings of importance, if possible, be executed on paper stretched on a drawing board in the usual manner, by applying gum at the edges only, and, instead of being removed and transferred to cardboard mounts, it would be safer for them to remain on the board and so be framed. In this way no adhesive preparation would be put at the back of the picture. For the same reason sunk cardboard mounts are advantageous, for it is necessary then to moisten only the edges of the picture with adhesive material.

ON THE METHOD OF CONDENSATION IN CALORIMETRY.*

By J. JOLY, B.E.,

Assistant to the Professor of Civil Engineering, Trinity College, Dublin.

A SUBSTANCE at the initial temperature t_1° of the atmosphere, suddenly immersed in a saturated vapour at the higher temperature t_2° , abstracts from it a quantity of heat equal to $WC(t_2^\circ - t_1^\circ)$, where C is the thermal capacity of the substance between the limits t_1° and t_2° , and W its weight. There is then a weight w of the vapour precipitated, so that—

$$WC(t_2^\circ - t_1^\circ) = w\lambda,$$

λ being the latent heat of the vapour.

By the observation of the weights and the temperatures, either c or λ may be the unknowns sought from the equation. The method is, in short, applicable to the determination of the specific heat of a substance or the latent heat of a vapour.

The paper contains an account of experiments illustrating the application of this method of condensation to the determination of the specific heats of substances. The condensation of steam is employed, its latent heat being accurately known, and its use affording a considerable range of temperature. Two forms of the apparatus employed are described. The calorimeter consists essentially of a vessel of thin metal in which the substance is suspended by a fine wire, the wire issuing through an aperture in the top of the vessel and reaching up to one arm of a balance. The vessel is so constructed that steam can be passed through it from a small boiler, displacing the air around the substance. The substance rests on a

light carrier of platinum wire provided with a little catch-water beneath to receive the drops of condensed water.

The manipulation involved is very simple. The substance, being placed on the carrier which depends from the balance, is counterpoised. The calorimeter is then closed around it, the suspending wire passing freely through the aperture provided. This aperture is formed in an absorptive material (plaster-of-paris), which ensures that it remains free of precipitated water. A thermometer reading to 1-10th degree C. is inserted in the calorimeter, and allowed to remain with the substance for an interval sufficient to secure close equilibrium of temperature. The thermometer being read is removed, and the calorimeter suddenly placed in connexion with the boiler, which supplies a brisk current of steam and fills it immediately. It then remains to note the increment of weight when the substance has finally attained the temperature of the vapour. This stage is revealed in the persistent equilibrium of the balance: t_2° is observed directly by a thermometer inserted in the boiler, or deduced by noting the height of the barometer and seeking the corresponding temperature of saturated steam from Regnault's tables. A correction is applied to the weight observed in experiment, necessitated by the difference of the weights of the displacement of the substance in air and in steam. In accurate experiments the value of λ is corrected according to Regnault's formula for its true value at t_2° .

The method is convenient for the reasons that it involves no preparations as in Bunsen's change of state method, no delicate thermometry, and the calorimeter being roomy permits of bodies of various shapes and bulks being dealt with. The apparatus, too, is of a simple and durable nature.

The experiments quoted in support of the method are (1) on the metallic elements, zinc, silver, lead, platinum, and aluminium. The results are in accord with those of Regnault, Bède, Mallet, &c. The degree of consistency between the experiments is greater than that attained in Regnault's researches. (2) On pure water sealed in thin glass bulbs. The results agree closely with the values deduced from Regnault's formula. (3) On mineral substances in various states of aggregation. It appears from these that the result is but little influenced by the extent of surface exposed to the steam.

The accuracy displayed by the method is explained on the probable supposition that the substance is throughout the period of heating coated with a film of water adiabatic and the external surface of which may be considered as appreciably that of the steam. The danger then of radiation error, that is, of steam condensing elsewhere than at the surface of the substance, is small. Condensation, in short, may be considered as taking place by abstraction of the energy of the molecule on impact with the water film.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 254.)

8. Test for Potassium.

WHEN testing for potassium we add a little perchloride of platinum to the drop which we have examined for crystals of gypsum. To effect this we make use of a little hook of platinum wire the end of which is sealed into a glass tube (loops are not so good as hooks for this purpose, because of the difficulty in cleaning them properly); we get a drop of the reagent on the end of the wire and then let it run into the middle of the drop under examination. The crystals of potassic chloroplatinate form in the course of a few minutes, generally along the edge of the drop; we can employ the time, while waiting, by pre-

* Abstract of a Paper read before the Royal Society, November 18th, 1886.

paring for the sodium and aluminium tests. When the crystals do not form quickly we can have recourse to alcohol, as has been already described.

The potassic chloroplatinate forms pale yellow octahedrons, very well formed, and having considerable refracting power. Their size varies from 10 to 30 microns. Concentrated solutions generally give a mass of small crystals, which often join together, forming twins or resembling the ace of clubs.

In solutions of chlorides the crystals form more easily, and are of smaller dimensions than in solutions of sulphates. A large excess of sulphuric acid interferes considerably with their formation.

Perchloride of platinum furnishes us with a micro-chemical reagent for detecting potassium, which leaves nothing to be desired. The reaction is certain, easy to observe, and as the presence of caesium and rubidium is very rare it is very characteristic and sensitive. It enables us to detect 0.0006 m.grm. of oxide of potassium. Hydrofluosilicic acid acts less rapidly, and the fluosilicate of potassium is much more difficult to recognise than the chloroplatinate.

The action of phosphomolybdic acid and phosphomolybdate of sodium is still slower than that of hydrofluosilicic acid; the separation of the potassic salt from a solution containing 2 per cent of potassic sulphate does not commence until the margin of the drop commences to get dry. But the crystals resemble those of potassic chloroplatinate, both as regards size and colour; the octahedric crystals of the two compounds are so much alike as to be taken one for the other. We find the same trefoil crystals in both kinds; however, the ordinary form of phosphomolybdate of potassium is the rhomboidal dodecahedron. Ceric sulphate added to solutions of potassic sulphate forms a double salt as quickly as perchloride of platinum, but not so well characterised either by form or colour. I shall refer to this double salt again in the following paragraph.

9. Test for Sodium.

The test for sodium, above all, presents great difficulties. I have long been hunting for a reagent which would indicate the presence of this metal; and at last my choice has fallen on cerous sulphate. This salt indicates, as does also hydrofluosilicic acid, the presence of potash as well as of soda. But whilst M. Boricky's reagent is more adapted to showing the presence of potassium rather than sodium, cerous sulphate acts in exactly the opposite manner. In fact, the double sodic salt appears long before the potassic compound. The double salts of ammonium and lithium are much more soluble; this property is possessed, but in a much higher degree, by the double calcic and magnesian salts, which furthermore form crystals of a totally different character. The yellow ceric sulphate gave no satisfactory results. We use the cerous sulphate in a concentrated solution, and place a drop of it at about 5 m.m. from the drop to be tested. We mix the two liquids by means of a fine glass rod; gradually we see forming in the cerous sulphate solution small facets of crystals, resembling desmine, which are nothing else but cerous sulphate, but at the edge, on the contrary, and especially if the quantity of sodic salt present is at all considerable, a zone thick and cloudy, coloured brown, and formed of the double sodic salt. In case potassium is present, we see appear in the middle of the zone just described another one coloured grey and granular in appearance, formed of the double potassic salt.

We can easily convince ourselves, by increasing the magnifying power to about 600 times or more, that these cloudy parts consist of little transparent grains, of hardly 2 microns in diameter (the sodic salt), and of spheroids a little larger, of about 5 to 8 microns in diameter (the potassic salt). These last have a slight resemblance to the starch granules of potatoes.

In neutral solutions containing less than one per cent

of alkaline sulphate, as well as in acid solutions, these phenomena do not show so distinctly. By placing the reagent quite close to the drop which is being tested, we see appear, after the lapse of several minutes, small spherical crystals, or, in more favourable circumstances, truncated rhombs of six or eight planes. These two forms belong to the cerous-potassic sulphate. As for the corresponding sodic salt, it shows under the form of short prisms about 3 to 5 microns in length.

The isolated crystals of cerous sulphate have the same general character of the cerous-sodic salt, but the size is about five or six times greater.

In solutions which do not contain more than a very little potassium and sodium, a large excess of sulphuric acid may entirely stop the formation of the above-mentioned double salts; in such a case we see appear spherical crystals, which are probably formed of an acid cerous sulphate.* The addition of magnesian or cupric acetate will help the reaction, but it is much better to take care, when attacking the mineral, that the sulphuric acid is almost entirely driven off. We can make use of cerous sulphate as a preliminary test for these two alkalies; in doubtful cases we then try the same drop, first with perchloride of platinum, and afterwards with hydrofluosilicic acid.

I much prefer to do the confirming test with perchloride of platinum; the use of hydrofluosilicic acid in the test for sodium being, in my mind, only a last resource, because it is impossible to be sure that the sodium does not come from the glass, except when using varnished plates, or when the precipitate comes down quickly and abundantly; it should be further remarked that this reaction is not very sensitive. In a solution containing 0.5 per cent of sodic sulphate, the cerous sulphate will cause the formation of the double salt after the lapse of about two minutes; in a solution of 0.15 per cent of sodic sulphate the reaction takes place only after five minutes, whilst the hydrofluosilicic acid gives only very feeble indications of a precipitate of the sodic salt in a drop of the same liquid after the lapse of twenty minutes. When operating with a solution containing 0.05 per cent of Glauber salt I could still notice the formation of the double sulphate after waiting ten minutes; hydrofluosilicic acid produced no effect whatever, even after waiting for more than half an hour. In extremely diluted solutions we can accelerate the reaction of the cerous sulphate by the application of gentle heat. We can often confirm the result by the colouration of the flame, or even try for sodium entirely by the wet way.

Lanthanic and didymic sulphates give rise, with the alkaline salts, to the same reactions as the cerous sulphate; but they are not so sensitive. It is easily seen that we can make use of a mixture known as *ceritic sulphate*, instead of pure cerous sulphate.†

Experiments with oxalic acid, ammoniacal oxalate, and potassic antimonate, did not give satisfactory results. The two first were not sufficiently sensitive, the third gave with calcic and magnesian salts thick pulverulent precipitates, which clouded the whole drop and thus hid the effect of the reagent on the sodic salt which took place later on. M. Streng's reagent (acetate of uranium) gives magnificent tetrahedrons of a yellow colour. Unfortunately the reaction is not very sensitive, in fact it is less so than that of hydrofluosilicic acid, and, further, it is interfered with by the least trace of free sulphuric acid.

(To be continued.)

* An excess of acid interferes less with the test for potassium than for sodium; we can thus, in acid solutions, find the potassium before the sodium, or the former only even when the solution contains a considerable quantity of sodium.

† This mixture is prepared by evaporating cerite with equal parts of sulphuric acid and water, and heating to dull redness. Treat this residue with four parts of cold water, filter, then boil the liquor; ceritic sulphate is precipitated, deprived of part of its water of crystallisation; warm this until it is anhydrous, and, when in the form of a fine powder, dissolve it in warm water.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 248.)

As further illustrating the differences in the results, the following table is presented :—

in the case of sample B, and results upon this sample (which contains the largest percentage of soluble) are much more discordant than for the others. Certain experiments were, therefore, made upon this sample.

1. 2 grms. were placed upon a dry filter and water added slowly and in small quantities until the filtrate

Percentage of results differing from mean not more than—
0·3 p.c. 0·5 p.c. 0·7 p.c. 1·0 p.c. 1·5 p.c. 1·3 p.c. 1·7 p.c.

Sample A.

Moisture	81	81	81	92	92	100	—
Soluble	80	100	—	—	—	—	—
Insoluble	40	54	74	80	100	—	—
Total	87	100	—	—	—	—	—

Sample B.

Moisture	73	73	82	92	92	92	100
Soluble	34	66	87	100	—	—	—
Insoluble	72	93	100	—	—	—	—
Total	87	87	100	—	—	—	—

Sample C.

Moisture	73	82	82	92	92	92	100
Soluble	94	100	—	—	—	—	—
Insoluble	40	60	66	74	94	100	—
Total	80	94	100	—	—	—	—

All determinations (not including moisture)

taken together 68 84 92 95 99 100 —

P₂O₅ determinations excluding insoluble .. 77 91 98 100 — — —

In connection with these results the following points may be noticed :—

1. The determinations of moisture, while somewhat better than those reported last year, are not as uniform, by any means, as could be desired.

2. The determinations of total P₂O₅ on the whole are satisfactory. The extreme variations between the highest and lowest results are for A, 0·83 per cent; for B, 0·83 per cent; for C, 0·82 per cent. Of the results upon A, 0·87 per cent differed from the average not more than 0·3 per cent; of B, 0·87 per cent, and of C, 0·80 per cent.

In order to determine as accurately as possible the content of total P₂O₅ in the samples, numerous special determinations were made by the Chairman of the Committee. Reagents and manipulation were proved satisfactory by determinations made upon solutions of C. P. hydro-disodic phosphate and of microcosmic salt, recrystallised, the strengths of which were proven by evaporation and ignition, and by precipitation with magnesia mixture. A series of molybdate determinations gave a mean error of less than 0·15 per cent.

(1) 0·5 gm. of sample was digested with 20 c.c. concentrated HCl, diluted and filtered.

(2) 0·5 gm. was covered with 5 c.c. saturated solution of Mg(NO₃)₂, evaporated, ignited, and dissolved as above.

The following results were obtained :—

	A.	B.	C.
1	19·00	18·48	17·71
.. .. .	18·94	18·60	17·80
.. .. .	18·96	18·54	17·76
2	18·89	18·50	17·70
.. .. .	18·97	18·61	17·81
.. .. .	18·92	18·49	17·72
Average	18·94	18·53	17·75
Average from Association chemists..	18·95	18·55	17·80

3. The determinations of soluble P₂O₅ are fairly satisfactory. The greatest extreme variation is 1·55 per cent

measured 200 c.c.; 2. 2 grms. treated as above until the filtrate measured 250 c.c.; 3. 2 grms. treated as above until the filtrate measured 300 c.c.; 4. 2 grms. treated as above until the filtrate measured 500 c.c.; 5. 2 grms. were placed in a beaker, about 150 c.c. of water added, stirred and rubbed with a stirring rod, filtered and washed until filtrate measured 300 c.c.

An aliquot was taken for determination in each case, after thorough shaking of the fluid and a small quantity of HCl added to clear up any possible cloudiness.

The results were as follows :—

	1.	2.	3.	4.	5.
Sample B, soluble } 10·52 11·35 11·56 11·55 10·21					
P ₂ O ₅ } 10·53 11·27 11·44 11·51 10·16					
Mean ..	10·58	11·31	11·50	11·53	10·18

These results indicate the necessity for slow washing with small quantities of water and for continuing the washing to the proper point. Acid reaction in the last drop of the filtrate was barely discernible in 2, after 250 c.c. of water had been used, and yet 50 c.c. more extracted nearly 0·20 per cent soluble P₂O₅.

4. The “insoluble” determinations are extremely unsatisfactory. The extreme variations are, for A, 1·64 per cent; for B, 0·91 per cent; and for C, 2·39 per cent. As upon this determination depends the estimation of the “available” P₂O₅, its importance is obvious. These discrepancies cannot be due to differences in the samples.

The close agreement in total P₂O₅ evidences strong probability that the samples were uniform. The same fact indicates that there is no fault in the method used for determining the P₂O₅ (molybdate and magnesia mixture). The difficulty is evidently in the character and manipulation of the citrate solution.

The committee is at a loss to know what to suggest in this connection, except it be to reiterate the cautions hitherto urged as to the strict neutrality and specific gravity of the citrate solution and careful attention to the specified temperature.

III. The committee recommends the continuance of the present general method for the determination of the

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

phosphoric acid, subject to such modifications in minor details as the Association may determine.

Respectfully submitted.

H. C. WHITE, Chairman.
E. H. JENKINS.
W. C. STUBBS.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To COLONEL SIR FRANCIS BOLTON, *Water Examiner,*
Metropolis Water Act, 1871.

London, November 5th, 1886.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be perfectly clear, bright, and well filtered.

The general character of the water supply of the month continued to be excellent. Notwithstanding the alteration in character of the season, the mean proportion of organic carbon in the Thames-derived supply, as compared with that of the previous month, had increased only from 0.132 part to 0.140 part in 100,000 parts of the water; while the maximum proportion in any one sample fell short even of the maximum of the previous month.

The series of bacteriological experiments, of which the particulars are given below, differ from those recorded in our previous monthly reports in the circumstance that the water subjected to infection had not been previously sterilised, but was infected at once as drawn from the service-pipe. Before commencing this series of experiments, we had to satisfy ourselves that the growths set up in the testing culture-fluid by the innocuous and presumably beneficent forms of microbe life naturally present in the water could be clearly distinguished from the growths set up by the purposely introduced morbid microbes, by the greater length of time needed for incubation, by the naked eye appearance of the growth when formed, and more particularly by its microscopic examination. Seventeen duplicate experiments were made, corresponding, of course, to thirty-four infections, mostly on different days from April 13th to April 29th, inclusive. In each infection a quantity of peptone-fluid, loaded with an active sporeless growth of *Bacillus anthracis*, was added to the freshly-drawn water, in the proportion, as nearly as might be, of 1-500th, or from the 1-400th to the 1-600th of its bulk. To contaminate to the same extent a single day's supply of the Thames water alone actually furnished

to London would require an addition thereto of considerably over a hundred thousand gallons of similar bacillus-charged animal fluid. The thirty-four tubes of infected water were kept at the temperature of the room, which, in the course of the experiments, varied from 57° to 63° F. (14° to 17.5° C.). After an interval of half an hour, and again after some considerably longer interval, tubes of sterilised culture-fluid were sown with the infected water, and subjected to incubation at 90° F. (32° C.) for periods of eighteen to twenty-four hours and longer.

The general result of this series of experiments is as follows:—1. The tubes of culture fluid, sown with the infected water within half-an-hour of its having been infected, were found in every one of the thirty-four instances to exhibit, after eighteen hours' incubation, a characteristic growth of bacillus. 2. In eighteen instances the sowings were not repeated until after an interval of six hours from the original infection of the water, and in every one of these instances the sowings were found to be infertile on incubation; or in no case was the life of the bacillus in the purposely infected water found to extend beyond six hours. 3. In the other sixteen instances successive sowings were made after intervals of three, four, and five hours. Here the results were irregular. For the most part the sowings made after but three and four hours' infection, and all but five out of sixteen of the sowings, made after five hours' infection, were found to be infertile. Further sowings, in the case of the five instances of more prolonged duration of vitality, were not repeated until the next morning, when they also were found in every case to be infertile.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 18th, 1886.

W. CROOKES, Esq., F.R.S., Vice-President, in the Chair.

MR. A. Wentworth Jones was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Horace Edward Brothers, Zaffre Cottage, Solden Hill, Stoke-on-Trent; Francis James Henderson Coutts, 61, East View, Turton Road, near Bolton; Tamemasa Haga, 1, Sadowara-machi, Itchomé, Tokyo, Japan; Michitada Kawakita, Engineering College, Tokyo, Japan; Stephen James Pentecost, Nottingham Road, New Basford, Nottingham; Henry Joshua Phillips, G.W.R. Laboratory, Swindon; P. Yeshwant Sheshadri, Jalua, Bombay, India; Tetsukichi Shimidzu, Noshomusho, Tokyo, Japan; William Phillips Thompson, 95, Shrewsbury Road, Birkenhead; Hikorukurō Yoshida, Science College, Imperial University, Tokyo, Japan.

The following were elected Fellows of the Society:—Messrs. B. F. Davenport, M.A., M.D.: W. Ralph Dodd; Laurence Hislop; A. B. Lyons, A.M., M.D.; James B. Readman; Alfred Rée; V. Phelps Richard; F. T. Shutt, B.A.; Edgar F. Smith, Ph.D.

The following papers were read:—

98. "*Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra.* Part. VIII.—*A Study of Coloured Substances and Dyes.*" By W. N. HARTLEY, F.R.S., Royal College, of Science, Dublin.

The author refers to a paper by Dr. Otto N. Witt, published in 1876, in which it is stated that the tinctorial characters of benzenoid compounds is conditional upon the simultaneous presence in the molecule of a colour-producing group and a salt-forming group of atoms; a group of atoms of the former kind being designated a *chromogen*, and of the latter a *chromophor*. He has studied the relation of the hydrocarbons to the more complex compounds which are colouring matters derived therefrom. It is shown that benzene and the derived hydrocarbons have the property of selecting and absorbing certain rays of the spectrum, and may thus be regarded as coloured bodies, the colours of which are too subtle for the eye to perceive them. By certain reactions, two or more benzenes may be linked in such a way that the rate of vibration of the new molecule is reduced so that it absorbs rays within the region of visibility. That which has been called a chromogen is an invisibly coloured substance, and that which is termed a chromophor is an atom or group of atoms capable of so reacting as to reduce the rate of vibration of the molecule, with the result that it absorbs rays of no higher refrangibility than the violet. Under certain conditions oxygen and nitrogen are chromophors, hence also hydroxyl and nitroxyl.

The spectrum measurements of a number of nearly related dyes and colouring matters are given, together with diagrams indicating their molecular vibrations.

The modification seen in the curve of benzene when an alkyl radicle displaces hydrogen consists in three out of the four absorption-bands being merged in one, and the rate of vibration of the absorbed rays is less.

When a body like triphenylmethane is examined, the absorption curve has much of the general character of that of benzene, but the modifications which it has undergone are much like what one might expect from its constitution. First, there is one broad band of absorption, with just an indication of a second being merged in this. Secondly, a great increase in the amplitude of the vibrations. Thirdly, the rate of vibration of the absorbed rays is greatly reduced.

When magenta, Hofmann's violet, and iodine-green are examined, it is seen that the curves are modifications of that of triphenylmethane; they follow each other closely, but the molecule of greatest mass transmits least light, and the light is composed of rays vibrating with least rapidity, thus indicating a greater amplitude and less rapidity of vibration of the molecule.

Azobenzene and a number of its derivatives of very varied constitution exhibit curves remarkably similar.

It is remarked that when absorption takes place in the visible region the ultra-violet rays are generally completely absorbed.

99. *Spectroscopic Notes on the Carbohydrates and Albumenoids from Grain.* By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

According to C. v. Naegeli ("Theorie der Gährung") fermentation is a process which may be described as the transference to fermentable matter of the molecular, or rather intra-molecular, vibrations of the different constituent substances entering into the composition of living protoplasm (which remains itself unchanged in composition), and hence the equilibrium of the molecules of the fermentable matter becomes so disturbed as to cause their resolution into simpler molecules. The author has had recourse to spectrum observations, in order to obtain, if possible, some information as to the mode and rate of vibration of the molecules of the bodies which initiate and participate in fermentative changes.

It is pointed out that animal albumens of various kinds examined by M. L. Soret are distinguished by absorption-bands produced by small thicknesses of dilute solutions, while the albumenoids invertase and diastase, and the water in which yeast has been washed, afford solutions which are very diactinic, and as far as could be ascertained do not exhibit absorption-bands. Moreover, gelatin is very diactinic when quite pure, and so also are the carbo-

hydrates starch, cane-sugar, and glucose. It does not therefore appear that there is anything in the mode and rate of vibrations of invertase which is incompatible with a transference of its vibrations to glucose, nor of the vibrations of diastase to starch; hence it is possible that some material within the yeast cell may communicate its motion to the sugar outside of it, and so resolve the complex molecule into simpler molecules. Putting the theory of fermentation on one side, it is of interest to know that the facility with which the ultra-violet rays traverse solutions of the carbohydrates is quite in accord with what we know of their constitution, notwithstanding the complexity of their molecules. It is, further, no less interesting to know that the albumenoids associated with the carbohydrates are evidently of very different constitution from those found in the animal organism. It is pointed out that gelatin dry plates very rarely receive impressions of rays of higher refrangibility than 2146, and this is due to some slight impurity in the gelatin, since some specimens of gelatin transmit the line of zinc 2024.

DISCUSSION.

Mr. SPILLER, referring to the differences in sensibility of gelatin plates to the most refrangible rays commented on by Prof. Hartley, said that, owing to the difficulty experienced in getting silver bromide emulsion to set and dry sufficiently rapidly in summer time, it had sometimes been the practice of makers to add a minute proportion of chrome-alum: this might account for some of the differences observed.

Prof. HARTLEY said that he had long thought that the soluble bromides had not been completely washed out; but as plates prepared with special care for him by Messrs. Mawson and Swan had also manifested the differences described, he now thought that they were probably due to actual differences—some minute impurity—in the gelatin used at different times in preparing the plates.

100. *"Preliminary Note on the Electrolysis of Ammonic Sulphate."* By HERBERT MCLEOD, F.R.S.

When a neutral solution of ammoniac sulphate is electrolysed in a U-tube provided with platinum plates as electrodes, nearly pure oxygen is evolved at the positive pole and hydrogen at the negative. For 1 volume of gas from the positive pole, a quantity varying between 4.7 and 5.4 volumes is evolved from the negative pole. A small amount of ozone is produced. On mixing together the electrolysed liquid at the poles a strongly alkaline liquid is obtained, containing a considerable quantity of "active" oxygen. When the liquid is first neutralised with sulphuric acid, then treated with excess of baric chloride, and the baric sulphate filtered off, the liquid deposits baric sulphate on boiling,—an indication of the presence of persulphuric acid in the solution.

When sulphuric acid that has been electrolysed is exactly neutralised with baric hydrate, the precipitate filtered off, and the liquid boiled, baric sulphate is precipitated; at the same time the liquid becomes acid, and a further quantity of baric sulphate is thrown down on the addition of baric chloride.

DISCUSSION.

In reply to a question from the President, Professor MCLEOD said that Faraday, in the experiments which gave results differing from those now described, had used an alkaline solution of ammonium sulphate in ammonia.

Dr. MESSEL asked if the deficiency in oxygen might not be due to the formation of hydrogen peroxide. In experiments on the electrolysis of sulphuric acid solution (with a current of 60 ampères), he had at all events observed the characteristic colour on application of the chromic acid and ether test.

Prof. MCLEOD said that he had always failed to detect hydrogen peroxide.

101. *"The Preparation and Hydrolysis of Hydrocyanides of the Diketones."* By FRANCIS R. JAPP, F.R.S., and N. H. J. MILLER, Ph.D.

The authors have attempted to hydrolyse Zinin's benzil-dihydrocyanide, $C_{14}H_{10}(OH)_2(CN)_2$, by means of concentrated chlorhydric acid, but without success. However, by dissolving benzil in alcohol, adding an excess of hydrogen cyanide, saturating the liquid with hydrogen chloride, and allowing the whole to stand for some weeks, a compound of the formula $C_{16}H_{12}N_2O$ was obtained, a reducing action having taken place. The compound crystallises from benzene in lustrous yellow flat needles or laminæ, melting at $196-197^\circ$. It is feebly basic, yielding a colourless hydrochloride which is decomposed by water. At the same time an acid of the formula $C_{16}H_{13}NO_4$ was obtained.

By the action of a strong aqueous solution of hydrogen cyanide upon phenanthraquinone, a dihydrocyanide, $C_{14}H_8(OH)_2(CN)_2$, corresponding with the benzil-derivative prepared by Zinin, was obtained. It crystallised in tufts of very slender needles, which when heated decomposed with evolution of hydrogen cyanide. Treated with fuming chlorhydric acid in the cold, this compound slowly evolves carbonic anhydride, and yields a mixture of two compounds, $C_{15}H_9NO$ (needles melting at 241°) and $C_{15}H_{11}NO_2$ (needles melting at 183°).

The compound $C_{15}H_9NO$ appears to be a lactam or lactim. It unites directly with metallic hydroxides to form salts, without elimination of water, and from the solutions of these salts mineral acids precipitate the original substance. It decomposes carbonates. The compound $C_{15}H_{11}NO_2$ is an acid; its salts appear to be isomeric with those of the compound $C_{15}H_9NO$, but are so unstable that satisfactory analytical figures could not be obtained.

In a preliminary note on the above subject (*Ber.* 16, 2418) the authors erroneously ascribed the formulæ $C_{16}H_{11}NO$ and $C_{16}H_{13}NO_2$ to those two compounds. The difference in percentage composition between the C_{15} and C_{16} formulæ is very slight, affecting chiefly the hydrogen, which was found too high in the earlier analyses.

102. "The Action of Salicylic Aldehyde on Sodium Succinate in presence of Acetic Anhydride." By GIBSON DYSON, Demonstrator of Chemistry, Normal School of Science, South Kensington.

By heating a mixture of 10 grms. sodium succinate, 15 grms. salicylic aldehyde, and 13 grms. acetic anhydride, in a sealed tube for 40 hours, at a temperature of $140^\circ C.$, the author obtained a substance having the composition $C_{18}H_{10}O_4$, to which he has given the name "*Dicoumarine*." It is an extremely stable body, insoluble in water, ether, alcohol, benzene, and chloroform, but soluble to a slight extent in hot glacial acetic acid, from which it separates on cooling in acicular crystals. It dissolves in a hot solution of sodium hydrate, but is reprecipitated unchanged on addition of an acid.

By acting on its alkaline solution with sodium amalgam, hydrodicoumaric acid, $C_{18}H_{14}O_5$, is formed. This acid, when heated at $130^\circ C.$, gives off a molecule of water, yielding an anhydride (hydrodicoumarine) $C_{18}H_{14}O_4$ (m. p. $256^\circ C.$); hydrodicoumaric acid also combines with bromine to form addition products. By further reduction of hydrodicoumaric acid, an acid having the composition $C_{18}H_{18}O_6$ is obtained. This *dihydrocoumaric acid* yields an anhydride, $C_{18}H_{14}O_4$, melting at $222-224^\circ C.$

Zwenger (*Annalen*, Sup. 8, 32), by reducing a saturated alcoholic solution of coumarine with sodium amalgam, obtained hydrocoumaric acid, $C_{18}H_{18}O_6$, which yields an anhydride, $C_{18}H_{14}O_4$, melting at $222^\circ C.$ The constitution assigned by Zwenger to his acid is the same as that given by the author to dihydrocoumaric acid; the two acids are, however, not identical. Both acids yield an anhydride $C_{18}H_{14}O_4$, melting at $222^\circ C.$ It is probable that we have here another case of isomerism similar to that observed by Perkin to exist between α - and β -coumaric acid.

103. "The Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide." By E. DIVERS, F.R.S., and T. HAGA.

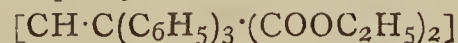
On decomposing silver nitrite with hydrogen sulphide, hydroxylamine is formed as chief product. Mercurous nitrite, supposed hitherto not to exist, has been prepared by the authors, and will be described in a future communication; it also yields hydroxylamine on treatment with hydrogen sulphide. In a preliminary note (*ante*) reference was made to the production of yellow crystals of unknown nature, together with metallic mercury and hydroxylamine, on treating mercurous nitrate with nitric oxide: having since prepared mercurous nitrite, the authors have now learned that these yellow crystals were this salt; and having ascertained that hydrogen sulphide converts it partly into hydroxylamine, they further recognised that the apparent formation of this base from mercurous *nitrate* and *nitric oxide* had really been its formation from mercurous *nitrite* and the *hydrogen sulphide* used to remove the mercury from the solution, as mercurous nitrite is soluble in nitric acid with but partial decomposition. The green solution prepared by mixing alkali nitrite with copper sulphate also yields hydroxylamine when treated with hydrogen sulphide. Alkali nitrites alone treated with hydrogen sulphide and then acidified, yield no hydroxylamine. The formation, here described, of hydroxylamine from the nitrites of the silver-mercury group of metals, is the only indisputable evidence there yet is of the conversion of an inorganic nitrite into hydroxylamine.

104. "Note on Some Double Thiosulphates." By J. B. COHEN, Ph.D., Assistant Lecturer on Chemistry, Owens College.

Rammelsberg found that by the action of copper sulphate upon a solution of potassium thiosulphate a cuprous potassium thiosulphate was formed of the composition $K_2S_2O_3 \cdot Cu_2S_2O_3 \cdot 2H_2O$. By increasing the proportions of potassium thiosulphate, a hydrated and anhydrous salt of the composition $Cu_2S_2O_3 \cdot 2K_2S_2O_3 \cdot 3H_2O$ and $Cu_2S_2O_3 \cdot 2K_2S_2O_3$, may be obtained, both of which give the same cuprous barium thiosulphate on addition of $BaCl_2$. An anhydrous silver potassium thiosulphate of the composition $K_2S_2O_3 \cdot 2Ag_2S_2O_3$ has also been prepared.

105. "Preliminary Note on the Action of Triphenylmethyl bromide on Ethyl Sodio-malonate." By GEORGE G. HENDERSON, M.A., B.Sc., Assistant to the Professor Chemistry, University of Glasgow.

When triphenylmethyl bromide, dissolved in absolute ether, is treated for some time with an equivalent quantity of ethylic sodio-malonate, a reaction gradually takes place: *ethylic triphenylmethyl-malonate*



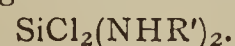
being formed. This substance crystallises from alcohol in colourless shining prismatic crystals which melt at 133.5° .

When hydrolysed with alcoholic potash, it is partially decomposed, carbon dioxide being split off, and the sodium salt of β -triphenylpropionic acid is formed. The acid itself $[C(C_6H_5)_3 \cdot CH_2 \cdot COOH]$ crystallises from alcohol in small colourless prisms which melt at 177° .

The sodium salt $[C_{21}H_{17}O_2Na \cdot H_2O]$ crystallises from water, in which it is very soluble, in long silky needles. The barium salt $[(C_{21}H_{17}O_2)_2Ba \cdot H_2O]$, is difficultly soluble in water, but readily soluble in alcohol, from which it separates in white crystals. The silver salt $[C_{21}H_{17}O_2Ag]$ is obtained as a white micro-crystalline precipitate, almost insoluble in water and alcohol.

106. "Action of Silicon Tetrachloride on Aromatic Amido-compounds." By ARTHUR HARDEN, B.Sc., Dalton Scholar in the Owens College.

The author finds that primary amines react with silicon tetrachloride, forming diamines of the formula



He has prepared such compounds from aniline, ortho-toluidine, isoxylidine, and betanaphthylamine.

Pyridine and quinoline form the additive compounds, $2C_5H_5N \cdot SiCl_4$, $2C_9H_7N \cdot SiCl_4$.

At the next meeting, on December 2nd, there will be a ballot for the election of Fellows, and the following Papers will be read:—"Bismuthates," by M. M. P. Muir. "The Action of Inorganic Compounds on Living Matter," by James Blake, M.D. "Morindin and Morindon," by T. E. Thorpe, F.R.S., and A. T. Greenal.

NOTICES OF BOOKS.

Heroes of Science: Physicists. By WILLIAM GARNETT, M.A., D.C.L. London: Society for Promoting Christian Knowledge. New York: E. and J. B. Young and Co.

HEROES are generally taken to be men who have distinguished themselves by acts of personal bravery when on the battle-field, or in other circumstances of great danger. But there is another class of heroes not often so well known to the public, and amongst this class heroes of science are most certainly to be found,—men who have devoted their whole lives with untiring energy to the solution of the problems and secrets of Nature, so that the world at large might derive benefit therefrom.

The book which now lies before us gives, in a most interesting manner, the lives of some of the more celebrated workers in chemical and electrical science, such as Benjamin Franklin, Henry Cavendish, Michael Faraday, &c.

The biography of Benjamin Franklin shows what a marvellous capacity he had for devoting himself thoroughly to quite different subjects when the necessity arose: thus we find him as a printer, a soldier, a politician, and a scientific experimenter of the first rank.

One of the drawbacks to Henry Cavendish was his extreme shyness, and his aversion to female society of any kind; he was entirely wrapped up in his experiments, and had comparatively little communication with the outside world. Dr. Wilson sums up Cavendish's view of life as follows:—

"His theory of the universe seems to have been that it consisted *solely* of a multitude of objects which could be weighed, numbered, and measured; and the vocation to which he considered himself called was to weigh, number, and measure as many of these objects as his allotted three score years and ten would permit. This conviction biassed all his doings—alike his great scientific enterprises and the petty details of his daily life. *Panta metro, kai arithmo kai stathmo* was his motto, and in the microcosm of his own nature he tried to reflect and repeat the subjection to inflexible rule and the necessitated harmony which are the appointed conditions of the macrocosm of God's universe."

But the hero of science who stands out far beyond his fellows is Michael Faraday, and Mr. Garnett very justly remarks that "The work of Michael Faraday introduced a new era in the history of physical science," and in this biography we cannot fail to be struck with the originality, simplicity, and penetration of this king of experimenters, so admirably set forth in this book.

The other biographies are equally interesting and instructive, but space will not allow us at present to enlarge on them.

Twenty-second Annual Report of the Alumni Association; with the Exercises of the Sixty-fifth Commencement of the Philadelphia College of Pharmacy. Philadelphia. 1886.

THIS Report contains a great variety of matter, some of which is of general importance. In the opening address of Mr. C. D. Lowe we find reference to a curious speci-

men of nomenclature. "A lady wanted to purchase some dog oil." This strange name is not italicised or put in quotation marks, but stands as an ordinary and intelligible term. But for the incidental remark in a following sentence, "commonly called sweet oil," we should have suspected that this barbarous term might mean Dippel's *oleum animale*."

A lecture delivered by Prof. F. Woodbury, M.D., on "Things Material and Immaterial," contains passages which in the eyes of most scientific men will seem to border upon the heretical. What shall we say of the following quotation from Prof. Tyndall?—"Inasmuch as it is still in its hypothetical stage, the ban of exclusion ought to fall upon the doctrine of Evolution." Surely such an utterance comes with scant grace from him who delivered the memorable "Belfast Address"; scantier still if we remember how many of the evidences which at that date were still hypothetical have since been absolutely demonstrated.

Dr. Miller commented very needfully on a label calculated to do much mischief:—"I saw an ounce bottle of sulphate of morphine with a label the upper portion of which said sulphate of morphine in tolerably large letters, then there was the usual vignette in the centre, and below the vignette it read 'Quinine Manufacturing Company,' and the word, in large letters, 'Quinine' immediately underneath the sulphate."

The law of negligence, as it relates to compounding medicines, is expounded at some length by W. E. Tolan, of the Philadelphia Bar. With one decision which he quotes we cannot for one moment agree. The defendants in a certain case sold antimony sulphide for manganese peroxide. The purchaser used it along with potassium chlorate for generating oxygen, and was severely injured by the explosion which ensued. Yet the defendant was held free from blame. This decision, as it was pointed out in the discussion, is the more inequitable since the preparation of oxygen along with potassium chlorate is perhaps the most common use to which manganese dioxide is put when bought in retail quantities.

Dr. J. J. Reese, Professor of Medical Jurisprudence and Toxicology in the University of Pennsylvania, gave a very interesting lecture on "Some Points in Toxicology." He brought forward a point which may in some cases complicate toxicological investigations, and of which an instance had come under his notice. Some person dies a natural death. An evil-minded being, having access to the body after death, introduces a solution of some poison into the stomach through a tube. He allows a couple of months to pass over, and then spreads a report that there has been foul play. The body is exhumed, and the poison is detected in the organs examined. The motive is, of course, to bring into condemnation some person who has been in the company of the deceased prior to or during his last illness. It has been found, by direct experiment upon the bodies of dead dogs, that arsenic, tartar emetic, and corrosive sublimate thus introduced may traverse the coats of the stomach, and may, after the lapse of three, six, or eight weeks, be detected in the liver, the kidneys, and the heart. Christison admitted the possibility of this crime.

In the subsequent discussion mention is made of the fact that arsenic (doubtless arsenious acid) is fifty times more soluble if boiled in water than if treated with cold water. In this manner about 600 persons are said to have been poisoned in Vienna.

A Set of Chemical Labels for the Laboratory, Alphabetically Arranged. By PHILIP HARRIS and Co., Bull Ring, Birmingham.

THESE labels are printed in a very bold, distinct type, each having the empirical formula above the name, and below it the rational formula. Besides labels for the ordinary reagents, there are others for the principal

standard solutions used in volumetric analysis, blanks being left for the value of a c.c. and for the number of grammes per litre of the solid substance.

This set of labels will be found decidedly useful in the laboratory.

CORRESPONDENCE.

AN EXAMINATION PUZZLE.

To the Editor of the Chemical News.

SIR,—The question stated below was set at an examination in one of the Government Departments upon a Laboratory Course on the analysis of substances containing only one metal and one acid. Can any of your readers kindly tell me how x could have miscondacted itself in the manner stated. The italics are mine.—I am, &c.,

A.X.

November 22, 1886.

A substance, x , dissolves in water and the solution is *alkaline* to test-paper; it gives no precipitate with hydrochloric acid and sulphuretted hydrogen, but a flocculent colourless precipitate with *ammonia*, which is unaltered by ammonium sulphide. The filtrate from this precipitate gives no further precipitate with ammonium carbonate, sodium phosphate, or *platinum chloride*. What substances behave like x , and how can you distinguish between them?

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 19, November 8, 1886.

Thermic Researches on the Reactions between Ammonia and the Magnesium Salts.—M. Berthelot.—The association of a metallic oxide such as magnesia with ammonia gives rise to the formation of a complex alkali, analogous to the oxides of tetramethyl-ammonium, possessing an energy superior to that of the metallic oxide, and comparable to that of the most powerful alkalies.

Report Presented on behalf of the Chemical Section on the Researches of M. Moissan relating to the Isolation of Fluorine.—M. Debray.—This report gives a summary of the history of fluorine from the first recognition of its nature by Davy in 1813. It describes the attempts at its isolation made by Davy himself, by the Brothers Knox, and by Louyet, who fell a victim to the poisonous fumes which he inhaled. Faraday, Gore, and Frémy took up the problem in succession, but it was not ultimately solved until M. Moissan took it in hand. The report describes his experiments, which have already appeared in the CHEMICAL NEWS, and cites the arguments by which he shows the nature of the gas obtained. The Section concludes, after witnessing the repetition of his experiments, that the gas obtained by the electrolysis of anhydrous hydrofluoric acid is certainly fluorine. They remark that the history of this body enters thus into a new phase.

General Methods of Crystallisation by Diffusion. Ch. E. Guignet.—The author has undertaken a generalisation of the beautiful experiments of the elder Becquerel on the slow actions set up between two liquids separated

by a membrane, a porous septum, or even a glass tube provided with a slit or a capillary orifice. He examines the physical and chemical actions of a solid diffusing itself into a liquid and the corresponding actions of one liquid diffusing itself into another.

Determination of the Neutralisation-Heats of the Malonic, Tartronic, and Malic Acids. Remarks on the Neutralisation-Heats of the Acids Homologous to Oxalic Acid and of the corresponding Hydroxylated Acids.—MM. H. Gal and E. Werner.—The authors give their results in the form of tables, from which it would appear that the neutralisation-heats of the homologous bibasic acids included in the tables decrease as the molecular weight increases. If we compare the development of heat produced in the neutralisation of oxalic, malonic, tartronic, succinic, malic, and tartaric acids with that furnished by the hydroxylated acids derived from them we see that the introduction of OH into oxalic, malonic, and succinic acids reduces their total neutralisation-heat by about two calories.

Synthesis of Conicine.—The author obtains a base, α -propylpyridine, which has the same properties, physical, chemical, and physiological, as conicine.

On Chemical Transformations induced by Solar Light.—E. Duclaux.—The author finds that solar light, aided sometimes, though not always, by solar heat, acts in the same manner as microbia, and, like them, rearranges complicated chemical molecules into simpler groups. Water and carbonic acid, products of combustion, form always parts of these groupings; but there are others, yet combustible and relatively stable under the influences which produce them, which appear as the residues, temporary or final, in the solar combustion of a great number of different bodies. These residues of solar action are almost always the same as the residues, temporary or final, of the action of the ferments.

A Novel Means of Preventing Secondary Fermentations in Industrial Alcoholic Fermentations.—U. Gayon and G. Dupetit.—The authors effect this object by the addition of minute doses of the salts of bismuth.

The Alcoholic Fermentation of Dextrine and Starch.—U. Gayon and E. Dubourg.—It is well known that the *Saccharomyces* are without action upon solutions of dextrine and upon starch-paste. A species of *Mucor*, however, has the double property of fixing water upon dextrine, and even upon starch, and causes these bodies to ferment. It does not invert cane-sugar or transform it into alcohol.

Reduction of Copper Sulphate during Fermentation.—H. Quantin.—Copper present in the must of grapes (added, e.g., as sulphate in the treatment of mildew) is eliminated as sulphide, and in that state is not attacked by the must.

Justus Liebig's Annalen der Chemie,
Vol. ccxxxvi., Parts 1 and 2.

Communications from the Physico-Chemical Laboratory of the University of Leipzig, comprising:—

Condensation of Thio-Urea and Acetacetic Ether.—Reinhold List.—The author examines the action of thio-urea upon acetacetic ether, the formation of thio-methyl-uracil, its derivative salts and ethers, and finally his experiments made to ascertain its constitution.

Nitro-derivatives of Methyl-uracil.—Albin Köehler.—It appears that strong nitric acids converts methyl-uracil into nitro-uracil carbonic acid, which gives off carbonic acid, forming nitro-uracil. On treating nitro-uracil carbonic acid in an alcoholic solution with hydrochloric acid there is formed nitro-uracil carbonic ether. Tin and hydrochloric acid reduce nitro-uracil carbonic acid to amido-uracil carbonic acid. Nitro-uracil carbonic ether is reduced by tin and

hydrochloric acid to a mixture of amido and oxyuracil carbonic ether. On saponifying this product there is obtained amido-uracil carbonic acid. The latter passes by splitting off carbonic acid into amido-uracil. Methyl-uracil is converted by fuming nitric acid and strong sulphuric acid into nitro-uracil.

New Mode of the Formation of Dibrom- and Dichlor-barbituric Acids.—R. Behrend.—This memoir does not admit of useful abridgment.

Communications from the Chemical Laboratory of the University of Würzburg.—These comprise papers by L. Knorr on synthetic experiments with acetacetic ether; by E. Fischer, on the synthesis of indol-derivatives, and on indols from phenyl-hydrazine; by Jos. Degen, on indoles from methyl-phenyl-hydrazine; by Anton Roder, on indoles from met-hydrazine benzoic ether; by Adolf Schlieper, on indoles from β -naphthyl-hydrazine; by Carl Bulow, on phthalyl-acetacetic ether and on certain compounds of phenyl-hydrazine; and by E. Fischer, notices on the hydrazines.

On the so-called α -Thiophenic Acid and its Relation to the two Normal Carbonic Acids of Thiophene.—Victor Meyer.—The two acids are quite distinct in their properties, their differences being constant and not removable by purification or transformation. All the derivatives of the two acids agree absolutely in their chemical properties and might be regarded as identical in the ordinary sense, only that every derivative from the α -acid yields α -acid on re-conversion, whilst every β -derivative yields the β -acid.

Communication from the Chemical Institute of the University of Bonn.—J. Brecht.—A memoir on acetyl-lävulenic acid and on the constitution of the γ -ketonic acids.

Journal für Praktische Chemie.
New Series, Vol. xxxiv., Parts 4 and 5.

Action of Aluminium Bromide upon Ethylene and the Bromides of the "Limit Alcohols."—G. Gustavson.—The author describes the preparation and properties of hydrocarbon-aluminium bromide, the action of ethyl bromide upon aluminium bromide; the behaviour of brom-ethyl upon hydrocarbon-aluminium bromide; the action of primary and secondary propyl-bromide upon hydrocarbon-aluminium bromide and aluminium bromide and the behaviour of isobutyl-bromide with the same bodies.

Communications on Germanium.—Clemens Winkler.—A very full account of the occurrence, properties, and combinations of this new element.

Contributions to a knowledge of the Hydrated Sodium Sulphides.—C. Göttig.—On treating a moderately concentrated solution of sodium hydroxide in strong alcohol with hydrogen sulphide there is formed, first, the compound $\text{Na}_2\text{S} + 6\text{H}_2\text{O}$; then when the solution is poorer in water $2\text{Na}_2\text{S} + 11\text{H}_2\text{O}$, and, under certain circumstances, the sulphide $\text{Na}_2\text{S} + 5\text{H}_2\text{O}$; all which substances disappear again on the prolonged action of hydrogen sulphide.

The Volatile Fatty Acids occurring in Commercial Lupuline.—J. Ossipow.—The author traces butyric acid, one of the two valerianic acids, or isopropyl-acetic acid.

Revue Universelle des Mines, de la Metallurgie, &c.,
Vol. xx., No. 1, July and August, 1886.

Note on the De-incrustation of Belleville Steam-Boilers.—C. Quéhant.

Corrosion and Incrustation of Boilers; Protection by Zinc.—Louis Canon.

In both these papers the use of metallic zinc is recommended.

Determination of Nitrogen in Coal and Coke.—From the *Zeitschrift f. Anal. Chemie.*

Electrolysis in Metallurgy.—A. Zoppetti.—The conclusion of a voluminous memoir not capable of useful abstraction.

Volumetric Determination of Sulphur in Sulphides which can be Decomposed by Hydrochloric or Sulphuric Acid.—F. Weil.—From the *Comptes Rendus*.

The Kjeldahl Process for the Determination of Nitrogen in Organic Matter.—L. L. de Koninck.—A summary of the Kjeldahl process and of the modifications in it which have been proposed.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. 4th Série. Vol. i., No. 8, August, 1886.

Discovery of a New Element.—Clemens Winkler.—Already noticed.

MISCELLANEOUS.

Cantor Lectures.—The first course of Cantor lectures at the Society of Arts is announced to be on the "Principles and Practice of Ornamental Design," by Lewis Foreman Day. The first lecture, on November 29th, will deal with the anatomy of pattern. The subject of the second and third lectures will be the distribution of ornamental design and the fitness of ornamental form respectively, while the fourth and concluding lecture will treat of natural form and ornamental treatment. These lectures are open to members of the Society of Arts, who have also the privilege of introducing friends. A limited number of tickets are available for the use of art-workers, actually employed in any handicraft connected with the decorative arts. Application for them should be made to the secretary of the Society.

What we Drink.—On Friday last Mr. E. Godwin Clayton gave a lecture, at St. James's Hall, entitled "What we Drink." After commencing with some general observations and setting forth the merits and demerits of various kinds of drink, he gave an interesting sketch of the history of wine, and stated that the natural amount of alcohol in wine was 10 per cent, but some, such as sherry and port, contained as much as 20 and 21 per cent. The least fortified wine is Madeira, which is very rich and of excellent flavour; in fact the lecturer stated that Madeira is the only wine that can now be relied upon for absolute purity; and curiously enough, in spite of this, although the population in England since 1819 has nearly doubled, the importation of Madeira has fallen from 750,000 gallons in 1819 to about 100,000 gallons in 1885. Tea he regarded as very refreshing, although we think that when drunk in large quantity, as is the present custom, it has almost as bad an effect on some persons as an excess of alcohol has on others. The habitual use of spirits is no doubt very prejudicial, and we think most people will agree with Mr. Clayton that the most refreshing and least hurtful drink for the general mass of English people is a glass of beer.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—London Institution, 5.

Medical, 8.30.

Society of Arts, 8. (Cantor Lectures). "The Principle and Practice of Ornamental Design," by Lewis Foreman Day.

TUESDAY, 30th.—Institution of Civil Engineers, 8.

Royal, 4. (Anniversary).

WEDNESDAY, Dec. 1st.—Society of Arts, 8. Adjourned Discussion on Paper on "Sewage Disposal," by Dr. C. Meymott Tidy.

Geological, 8.30.

THURSDAY, 2nd.—Chemical, 8. Ballot for the Election of Fellows "Bismuthates," by M. M. P. Muir. "The Action of Inorganic Compounds on Living Matter," by James Blake, M.D. "Morindin and Morindon," by T. E. Thorpe, F.R.S., and A. J. Greenal, London Institution, 6.

FRIDAY, 3rd.—Geologists' Association 8.

THE CHEMICAL NEWS.

VOL. LIV. No. 1410.

TREATMENT OF PHOSPHORIC CRUDE IRON IN OPEN HEARTH FURNACES.*

By J. W. WAILES.

IF the treatment of phosphoric pig-iron be measured in its importance by the quantity of this material, compared with that which may be called for practical purposes non-phosphoric iron, it will possess an importance in Europe ten to twelve times greater than that of a process only calculated to deal with the purer kinds of crude metal; for it is roughly estimated that the deposits of ore yielding phosphoric pig-iron exceed by about ten or twelve to one those yielding non-phosphoric pig.

As all pig-iron, more or less, contains phosphorus, it will be necessary to draw a line between this phosphoric iron and what regarded as non-phosphoric iron. This line has been drawn within comparatively narrow limits by the great steel-making processes of Bessemer and Siemens prior to the introduction of the basic process of Thomas and Gilchrist.

The effect of phosphorus in wrought-iron and steel is to cause "cold-shortness," i.e., brittleness at ordinary temperatures. The amount of phosphorus that can be allowed in steel depends largely on the purpose for which the metal is intended, and on the amount and relative proportions of other elements the steel may contain. Hard steel for certain purposes has been found to answer well with 1 per cent, or even a little more phosphorus; but it is generally allowed that where soft and ductile metal is wanted the less phosphorus it contains the better.

As the great steel-making processes already alluded to remove very little of any phosphorus, pig-iron with not more of this element than could be allowed in the finished steel had to be selected. So that a line may be drawn at pig-iron with more than 1 per cent of phosphorus; though steel produced from such iron could only have a very limited consumption, and, as a matter of fact, half this quantity of phosphorus is quite as much as manufacturers care to deal with.

By the reducing process of the blast-furnace, the phosphoric acid found in the ore finds its way into the pig-iron, and there appears as little prospect as ever of producing non-phosphoric iron from phosphoric ore (to any commercial extent) as ever there was.

This part of the question, however, is not one coming within the scope of this paper; it is only intended to begin where the blast-furnace leaves off, and to consider the treatment of the crude metal as it is produced.

The whole of the pig-iron produced in the Midland Counties, unless from ore imported, contains more phosphorus than could be allowed in marketable steel. So that it is to some process with the power to eliminate phosphorus that the iron manufacturer of the Midlands must look in the future, as he has done in the past, for his occupation.

The introduction of the basic Bessemer process rendered the removal of phosphorus from pig-iron in its conversion into steel a thing of certainty and great commercial utility. It is not, however, contemplated to deal with this branch of the subject, but to confine the necessarily brief remarks to the open hearth mode of treatment.

Although, as has been stated, the great steel process required—before the introduction of the basic process—

crude iron free, or nearly free, from phosphorus, the puddling process has for over a century converted phosphoric pig-iron into wrought-iron, and in this conversion has removed 80 to 90 per cent of the phosphorus it contained.

At the head of the list must stand the well-known process of puddling, and it is only with the view of comparing it with another and really very similar process that it will here receive a brief description.

Diagram No. 3, fig. 1*, shows a longitudinal section of a common puddling furnace most generally in use in the Midland district, and fig. 2 an elevation of the same. In fig. 1: A, the fire grate; B, the hearth; C, the flue to the chimney. The process is as follows: The hearth (B) is first "fettled," fitted or formed with oxide of iron, and the pig-iron in quantities of from 4 to 5 cwts. charged in through the door, which is then closed, and the heat forced as rapidly as possible, the damper being kept open. In from 30 to 40 minutes the iron is melted, and the operation of puddling begins. The puddler takes a "rabble" (an iron bar with a paddle-shaped end), about 2 inches broad and bent at the end at right angles to the staff for a length of about 5 inches. The oxide of iron from the bottom and sides of the hearth melt up with the molten pig-iron, and the puddler thoroughly agitates it, so as to wash the iron with the fluid oxide. Ebullition commences, and the stirring is continued. A change now begins to be perceptible, the iron thickens and appears crumbly, shows signs of separating itself from the fluid oxide, and forming on the bottom. Heat is checked by lowering the dampers, and the spongy iron worked together and formed, with much skill and exertion, into balls of the desired size.

With a pair of tongs these balls are dexterously lifted from the furnace and conveyed to a hammer or press, where the cinder is expelled and the ball is forged into a rectangular block and, at the same heat, passed through rolls to form it into a bar of any required size. When cold, the bar is cut up and piled for further rolling.

The operation of puddling, which takes from 30 to 40 minutes after the pig-iron is melted, is one demanding very great exertion, the puddler in hot weather working stripped to the waist and in a bath of perspiration.

It is reported that a celebrated iron manufacturer has said that only fools would become puddlers; but this certainly is not true in the Midland Counties. The operation requires considerable skill and attention, and, as a rule, the puddlers are a class deserving both sympathy and respect. The work is divided between two men, a first and second hand, the latter taking the earlier part of the operation. Six heats is the usual turns work.

The chemical reactions that take place during the conversion of crude iron into wrought-iron will readily be gathered from a glance at diagram No. 2. In the changes shown, the time is placed in the left-hand column and remarks in the one opposite. The various elements are shown in the same colours in all the diagrams of both iron and steel reactions, viz., carbon, brown-silicon, yellow, sulphur, blue, phosphorus, red, manganese, purple.

Innumerable modifications of the puddling furnace, and the means of carrying out the operation of puddling, have from time to time come to the front, and met with varying success. These modifications appear to divide themselves into two principal groups.

1. Where the manual labour is superseded by the application of mechanical motion to the rabble.
2. Where it is sought to obtain the same end by imparting rotary motion to the melting chamber of the furnace.

In both these plans, and indeed in all the modifications of the puddling furnace, the great difficulty underlying everything has been the want of heat. Puddling is really

* A Paper read before the British Association, Birmingham Meeting, Section B.

* These have reference to the diagrams exhibited during the reading of the paper.

nothing more than a device rendered necessary by want of sufficient heat. When the molten crude iron has parted with a large portion of its alloys, the heat in the puddling furnace is insufficient to hold the purified iron in a molten condition, and it therefore becomes necessary to take it from the furnace in a spongy state.

Having briefly sketched the puddling furnace, and given a few of its reactions, a comparison can readily be made with the process now to be described. Diagram No. 3 represents a plan and elevation of the "Batho Furnace," an improved form of the Siemens regenerative furnace.

Generally considered, the principal character of this invention is the getting rid of the idea of a furnace as a building.

A simple mechanical contrivance is substituted for the mass of masonry, bound together with iron stays and props. In the contrivance before you four wrought-iron cases form the regenerative stoves and a fifth circular case the melting vessel. The stoves are connected to the vessel by means of pipes, lined with heat-resisting material. This furnace, or apparatus, has been described by Mr. F. W. Dick, of the Steel Company of Scotland, in a paper read before the Iron and Steel Institute at the Chester meeting. The stove cases are lined with a course of bricks, backed up with burnt ashes; this material forming a good non-conductor, and having the further important recommendation of being cheap.

There is much advantage in this separate system of regenerator. The very nature of the regenerative furnace demands that these shall be continually heated and cooled, causing corresponding expansion and contraction, often producing in the old form of regenerative furnace (where the regenerators are built in a solid block of masonry) cracks, allowing the gas and air to mix, and causing great trouble and loss.

In keeping these chambers tall, and placing the chequer bricks pretty open, the heat is collected and given back with as little obstruction to the currents as possible, thus securing the most rapid action of which the furnace is capable.

The melting vessel is lined with basic material, and covered with a lid of silica bricks, enclosed in a strong iron ring. This lid is suspended from girders, and does not rest on the sides of the melting vessel, and by means of small rollers can be run back so as to open the vessel when repairs are necessary.

An aperture through the side of the vessel allows the inflow of gas, and directly over this the column of air flows through an opening in the lid, deflecting the gas, which acts like a blowpipe on the material under treatment. Combustion thus obtained is very rapid, and, as the lid has only to resist the radiated heat, it is not cut or melted, as is the case when the flame breaks against any part of a silica lining.

Any contact between the acid lid and the basic sides of the melting vessel, at the heat necessary to purify the charge, would result in the rapid destruction of the parts coming together: a small space, however, is found quite sufficient to overcome any difficulty of this kind, and it is only necessary to keep the two materials $\frac{1}{4}$ of an inch apart.

The composition and application of the basic lining to the vessel is as follows:—

Lining is composed of highly burnt dolomitic limestone, called—

Shrunk lime	about 77 parts by weight.
Retort carbon	" 12 "
Fine wire cuttings ..	" 6 "
Oxide of iron	" 5 "

This material is ground up to a moderately fine powder, and mixed with sufficient tar to form it into a plastic mass, to allow of its being rammed round a mould placed in the interior of the chamber. The casing of the melting vessel is perforated with small holes about 6 inches apart,

through which a strand of an old wire rope is passed, and the wire spread out to hold the lining to the casing securely.

Basic lining is not easily obtained in a form allowing of its being used as a building material. It will, however, be easily seen, that in the form of the apparatus under consideration the difficulty attending the application of the lining is reduced to a minimum.

The use of the wire as a mixture in the lining may be best explained by stating that it is used for very much the same reason that hair is used in plaster; it prevents the plaster cracking and falling from the walls.

The melting vessel may be made of any capacity. The one in use at the Patent Shaft and Axletree Co.'s Works takes a charge of 5 tons, but vessels up to 8 or 10 tons will be adopted by this Company in future.

One advantage of considerable importance in the form of the apparatus is that heat may be urged as fully as possible as soon as gas is turned on, without fear of damage due to rapid expansion; the slow annealing necessary in the ordinary form of furnace is of no importance.

The mode of working is perfectly simple, and is as follows:—Full heat being obtained, which may be done in twelve or eighteen hours from the time gas is first turned on, lime and oxide of iron are put on the bottom and sides of the hearth of the melting vessel, and the charge of any kind of scrap and phosphoric iron put in, and the door closed. The charge is melted in from three and a half to four hours, and a slag formed by the melting oxide of iron and lime, and reaction commences. This is kept up by the occasional addition of ore and lime, till the boiling ceases in about eight hours after the charge is put into the vessel. Samples are taken during the latter part of the operation, hammered, and quenched in water. These samples are then bent or broken. A little experience soon enables the operator to determine the condition of the charge. The addition, at the end of the charge, of a little pig-iron containing a good percentage of carbon, has the effect of again starting a rapid boil, which lasts for twenty to thirty minutes. This plan produces good results, and removes the traces of phosphorus.

Manganese is thrown into the bath, and the charge tapped in the usual way.

From seven and a half to ten hours are occupied over the charge from first to last, probably a little more time than would be taken over an acid charge.

In performing any chemical operation the cleanliness of the vessel employed is a thing of great importance, and the purification of phosphoric iron in this vessel is no exception. Especially is it important to keep the vessel free from any acid matter. This important condition is obtained by keeping all acid lining entirely out of the vessel, and directing the flame away from the lid.

In comparing the two open hearth means of purifying phosphoric iron, it will at once be seen that the latter will accomplish the desired end far more thoroughly than the former, for the simple reason that the more perfect the heat the more perfect the reaction. To quote Mr. Stead, from a paper already referred to, "The conditions required for the elimination of phosphorus are the same in every dephosphorising process. In fact, the law is established that dephosphorisation is always effected when fluid iron is brought into contact with an oxidising base, which must be in excess and fluid."

This being so it follows, as a matter of course, that the more perfectly the conditions can be fulfilled, the better—or at any rate the purer—the resultant.

The table of reactions shown on diagram No. 4 sufficiently explains the process, and comparison can be at once made with the reactions obtained under similar conditions in the puddling furnace, shown by the tables, diagram No. 2.

It is quite certain that, by the process just described, ingot iron of the most perfect quality can be readily pro-

duced from crude iron containing a very high percentage of phosphorus. Indeed it is a question in the writer's mind if the amount of phosphorus in the pig is a thing of any moment, any more than carbon or silicon under other conditions.

The normal mechanical condition of this ingot iron—and by this is meant when it is as pure as can be made—gives a breaking strain of 24 to 27 tons per square inch, with an elongation in 6 inches of 25 to 30 per cent, and a reduction of area of 50 to 70 per cent.

In the Bingley Hall Exhibition the Patent Shaft Company show a small 6-inch ingot that has been drawn down at one end under the hammer. This will sufficiently serve to show the quality of this metal in regard to what may be called "hot test." It is an advantage to work the charge from the commencement with manganese, either in the pig or added as spiegel or ferro-manganese.

Time will not allow more than a few principal points being considered; but in comparing ingot metal with the bar obtained from puddling, it must not be forgotten that the imperfection of the latter has in it a point of no small practical value.

The fibres of the pure soft iron, arranged amongst the entangled slag in the puddled bars, prevent what is certainly a weakness in the purer homogeneous metal.

A patent fagotted axle—such as those made by the Patent Shaft Company, where the purest crude iron obtainable is used, and process of manufacture watched, and the numerous bars which go to form the fagot selected with great care—such an axle, if superficially cut with a sharp tool and then subjected to the shock of a falling weight, will bend and allow the fibre to open to the depth of the cut only.

If, however, any steel bar, no matter how good, be treated in the same way, complete fracture is the inevitable result.

It was not intended to consider in this paper any view of the pneumatic process of treating phosphoric iron (the basic Bessemer process). One word, however, may not be out of place. The oxidising base needed to eliminate the phosphorus in the Bessemer converter has to be obtained by the oxidation of part of the metallic charge. In the open hearth treatment the oxide is put in the vessel as oxide, and although the conditions may and must be the same in every dephosphorising process, the means employed in creating these conditions differ widely.

Periodically the users of soft steel receive a shock—a mysterious failure is reported and certain papers are full of articles and letters on the subject—a boiler-plate has cracked like a sheet of glass; chemical analysis shows—what must be regarded from that point of view—satisfactory material, or, perhaps, very pure material.

It is not the purpose of this very sketchy paper to advance any theory on this important point, but it is generally revealed on investigation that these failures occur in steel of one class, viz., very soft steel made by the Bessemer process, steel where the process has been pushed to its utmost limit and oxidation has been greatest.

That this is debateable ground the reports of many discussions fully testify.

In considering the mechanical properties of soft homogeneous iron, it appears only fair that this side of the question should be touched upon.

Ingot iron from the open hearth basic furnace in England has not had the test of time that Bessemer ingot iron has had, so that it is not just to say that it does not possess this element of uncertainty; but from all the opportunities the writer has had of forming an opinion on the subject, a good chemical composition may be relied upon for a correspondingly good mechanical result.

The following is a fairly typical charge made from 75 per cent of Staffordshire white and mottled cinder pig iron—containing 2·8 per cent of phosphorus—and 25 per cent of steel scrap:—

Carbon	0·12 per cent.
Silicon	nil „
Sulphur	0·02 „
Manganese	0·43 „
Phosphorus	0·028 „

This charge rolled into $\frac{7}{8}$ inch round bars gave a tensile strength of 25·7 tons. An elongation of eight inches of 26 per cent and a reduction of area at point of fracture of 68 per cent.

That the old puddling process is dying full of years and honours, after having wrought mighty things for the civilized world, is a fact beyond all doubt. What particular process shall take its place in the largest degree time alone will determine. For the process just described, it may be said that it hardly supersedes puddling, it only renders the manual labour unnecessary, and in another way does the work far more perfectly.

THE COMPOSITION OF HYDRATED SALTS.

By SPENCER U. PICKERING and P. G. SANFORD.

Some short time ago Maumené (CHEMICAL NEWS, liii. 146) drew attention in these columns to the views entertained by him concerning the proportions in which elementary substances combine. The formulæ which he would have us assign to various substances are far more complex than those which chemists have hitherto been willing to accept. According to him potassium peroxide is $K_{16}O_{39}$, sodium peroxide $Na_{16}O_{23}$, &c.; potassium hydrate $(K_2O)9(H_2O)_{47}$; and the conclusions which he draws from analyses of the hydrates of potassium, &c., he would extend to the hydrates of all salts, and deny that the water molecules present in them bear any simple numerical relation to the molecules of the salt (*Bull. de la Soc. Chem. de Paris*, December, 1885). Although these views are not likely to find a very ready acceptance amongst chemists, the careful analytical results on which they are founded must receive some explanation before they can in reason be rejected.

The facts which he signalises are, moreover, in accordance with our general experience. Few who have had occasion to prepare any hydrated metallic salts can have failed to observe the difficulty—and often, indeed, the impossibility—which there is in obtaining them with the theoretical percentage of water. To take, as an instance, the various salts prepared by Thomsen for his calorimetric determinations: out of fifty-seven different specimens* (*Thermo-chem.*, iii., 199) ten only contained the theoretical quantity of water, seven contained less water than their formulæ necessitated (on an average 0·08 H_2O less), while as many as forty contained more water than they should have, this excess amounting on an average to over 0·1 H_2O .

The explanation of this non-accordance of actual and theoretical results is, we believe, very simple. In the course of preparing several normally anhydrous salts, we have been much struck by the extent to which accidentally enclosed water is retained by them, in defiance of fine powdering and prolonged heating, at temperatures considerably above 100° C.

We have determined the amount retained in several instances by the salts: (1) after they had been exposed over sulphuric acid till constant in weight; (2) after treating at 100° till constant; (3) after a similar treatment at 200°. The salts consisted in most cases of preparations which had been passed through a sieve with thirty meshes to the inch, and which would not pass through one with sixty meshes to the inch; in one case finer sifted samples—(1) that passing through sixty but not through

* This number does not include some of the salts of the rarer metals where the discrepancies observed were very large.

Salt.	Water Contained in Crystals.			Medium sample after drying over H ₂ SO ₄ .	Fine Sample after drying over H ₂ SO ₄ .
	Coarse Sample after drying—				
	At 200° C.	At 100° C.	Over H ₂ SO ₄ .		
Sodium chloride	0·706 } 0·615 }	0·738 } 0·648 }	0·770 } 0·683 }		
Ditto, another sample ..			0·608 } 0·675 }	0·349 } 0·303 }	0·228 } 0·205 }
Sodium chloride, crystallised at 100° C.			0·721 } 0·769 }		
Sodium chloride, crystallised at low temperature—					
Crystals, large			0·310		
„ small			0·223		
Potassium chloride			0·749 } 0·761 }	0·337 } 0·303 }	0·321 } 0·343 }
Potassium chlorate			0·334 } 0·368 }		
Potassium sulphate			0·131 } 0·0904 }		
Potassium nitrate	Nil	Nil	Nil		

ninety, and (2) that passing through ninety—were also examined.

The results are given in the accompanying Table, and show how considerable may be the amount of water thus mechanically retained within the crystals of a salt.

What occurs with these normally anhydrous salts will undoubtedly occur in the case of hydrated salts also, and will fully account for the water percentage obtained on analysis being generally above the theoretical amount, especially when it is remembered that in very few cases is it possible to dry a hydrated salt previous to analysis in as effectual a manner as in even the least dried samples here taken. It must be owned that we have no means of determining the amount of combined water in a hydrated salt, and we can therefore draw no conclusions from any analytical results which are obtained.

In the case where the water present was greatest (potassium chloride) it amounted to as much as 0·76 per cent, or 0·03 H₂O. It varies considerably with the manner in which the sample is prepared. The specimen crystallised from a hot solution contained more water than that crystallised in the cold: this is probably due not to the direct influence of temperature, but to the former crystals being formed less regularly, and consequently offering more internal spaces in which some liquid may be enclosed.

The water contained varies to a very large extent, as might be supposed, with the nature of the salt. In the case of potassium nitrate it is practically *nil*. The same variation will undoubtedly exist with hydrated salts, and in some cases (though these are probably somewhat exceptional) no enclosed water may be present, and it will therefore be possible to obtain the hydrate with the theoretical percentage of water. This would appear to be the case with the sulphates of magnesium, copper, &c.

THE GOLDFIELDS OF BURMA.

By R. ROMANIS, D.Sc.

It has long been known that gold occurs in the river sands of Burma. The alluvial deposits of Lower Burma have long been exhausted, but those on the Chindwin in Upper Burma are still worked to a small extent, and there is a report of platinum having been found there.

Lately I have received two specimens of gold from Mr. R. C. Stevenson, the Deputy Commissioner of Mya-daung. They were found to the westward of Katha, the head quarter station, about 30 miles from the Irrawaddi, on the banks of the Meza, in the territory of a semi-independent chief,

the Wuntho Tsawbwa. The hills forming the valley of the Meza are a prolongation of those of the lower defile, which are auriferous in places. At Tigyang, where the Meza falls into the Irrawaddi, they are composed of schistose rock. I was told that this district was famed for its diamonds, but, as I expected, they turned out to be zircon. The specimens were brought to Katha by a native, who said that one had been obtained at the foot of a range of hills, and the other in the bed of the Meza.

(A) is in comparatively large irregular fragments with quartz embedded in some of them. Under the microscope I picked out a fragment of iridosmine and a crystal of chrome iron. It also contains copper pyrites, magnetic oxide of iron, and an ore of silver, a grey mineral which lost 49 per cent on ignition.

(A).

Gold	87·66
Silver	5·96
Copper pyrites	1·95
Quartz	1·09
Magnetic oxide of iron	0·32
Silver	1·54
Loss on ignition	1·48

(B) is in fine smooth grains containing little magnetic oxide. It left a residue insoluble in aqua regia, of about 17 per cent, of which about 7 per cent was iridosmine in bright flat grains mixed with a black mineral, apparently a platinum ore: the rest was zircon and quartz.

(B).

Gold	74·83
Silver	2·86
Platinum	2·53
Iridosmine	7·04
Zirconia	7·08
Silica by difference	5·66

100·00

Mr. Mathews, now officiating civil officer at Katha, has obtained details of the methods of working. These are three:—

I. Washing with water led from the mountain streams. A channel is made across one of the little level spots found at the foot of the hills, into which the stream is diverted for a few hours, then it is turned off and the deposit formed in hollows, excavated in the bottom, is examined by washing in wooden main dishes.

II. By long ditches dug before the rains; after the floods have subsided the deposit at the bottom is examined and the gold washed out.

III. By sinking shafts to the auriferous stratum, a thin layer of dark sandy soil mixed with stones, from 7 to 30 feet below the surface, and then tunnelling laterally for a few feet; no frames or props are used in these galleries.

The out-turn does not appear to be great. In one of the five townships in which gold is obtained the annual yield is between 7 and 8 lbs., but if the Californian system of "hydraulicking" were applied where the first two methods are in use great profits might be made, if the Aborigines, Kadu Shans, did not interfere, as they are certain to do.

ON THE SPECIFIC HEATS OF MINERALS.*

By J. JOLY, B.E.,

Assistant to the Professor of Civil Engineering, Trinity College, Dublin.

THE specific heat constant is serviceable as a means of mineral diagnosis. Its numerical value, primarily a function of the weights of the atoms present, admits of calculation to a close degree of approximation on an assumed chemical constitution, even in the case of the more complicated silicates. In a secondary degree experiment appears to show that the thermal capacity is variable with the degree of order prevailing in the molecular constitution of the mineral, tending to be a minimum in the well-crystallised substance. Thus the characteristics of roughness, opaqueness, and formlessness are accompanied with heat capacities greater than those accompanying lustre, transparency, and symmetry.

It would appear further that under one and the same crystalline form different specimens of the same mineral may exhibit quite distinct thermal capacities, not apparently accounted for directly by differences in chemical composition, but generally accompanied by difference in diaphaneity. This is shown in the cases of aquamarine and clouded beryl, sapphire and corundum, apatite, calcite, and oligoclase. This phenomenon of multiple thermal capacity is well marked also in the cases of sphalerite, pyrite, and galena, in which group of isometric sulphides there is also a numerical relation traceable between the values. The quantities, including the observations of other observers, being in continued proportion with one another. The specific heat of marcasite, the trimetric form of the disulphide of iron, enters this proportion. Thus, designating the specific heats after the initials of the minerals,

$$s_1 : s_2 :: p : m :: g_1 : g_2.$$

The phenomena observed seem to suggest the possibility of different molecular arrangements obtaining under the same crystalline form, and effecting the thermal freedom of the molecule to different extents, but in a definite way.

The specific heats, taken by the method of condensation, of a number of minerals and rocks are added in the paper.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 267.)

10. Test for Lithium.

LITHIUM is very easy to find in sulphate solutions, if we have been careful to eliminate all the gypsum as completely as possible, according to the method already explained. We precipitate the lithium as carbonate; the

crystals of this salt, which are very distinct, of rectangular section, and apparently monoclinic, are about 50 to 75 microns in length.

We might be led to confound these crystals with gypsum and with the double salts formed by the combination of carbonate of magnesium with the alkaline carbonates; but the lithia salt is distinguished from the above-mentioned calcium salt by the almost constant occurrence of rectangular crystals and by its solubility in weak sulphuric acid; as for the double magnesium salts, they never form except in the presence of an excess of an alkaline carbonate, while the relative proportion of lithic sulphate and potassic carbonate has no influence on the formation of lithic carbonate.

In magnesian solutions, provided we have not added too much alkaline carbonate, we cannot see any prismatic crystals of the double salt forming, except in the immediate neighbourhood of the reagent, and these have only a momentary existence, as they almost immediately decompose and form little grains of magnesian carbonate. The presence of phosphoric acid interferes considerably with the test for lithium in the form of carbonate; in fact the addition of a solution of a phosphate leads to the destruction of the lithic carbonate already formed.

11. Test for Barium and Strontium.

Barium and strontium are found in the form of sulphates, in the sediment which remains in the platinum crucible, after we have decanted the aqueous solution of sulphates; this sediment still contains gypsum, when the proportion of calcium in the mineral is sufficiently great; when warmed with concentrated sulphuric acid the sediment dissolves, and, on cooling, and by the absorption of water vapour, the liquid soon throws down the barium salt in the form of little crossed lenticular crystals of about 5 to 12 microns in length.

The strontic sulphate appears later. It first forms in little confused bundles of fine needles, analogous to those we observe when gypsum separates rapidly from an acid solution; little by little we see appear crossed crystals, the smaller of which might be confounded with those formed by sulphate of barium, while the more sharply defined are easy to recognise, since they are of much larger dimensions (20 to 30 microns wide and 30 to 45 microns long), and have a rather more complicated structure. They eventually form rhombs, generally rather cloudy, and slender at the ends (they owe their formation to the matting together of the crossed crystals); sometimes these latter unite, forming twins and double twins in the form of a cross.*

The gypsum which dissolves separates later on, first as needles collected in bundles or rosettes, and finally in its ordinary form.

12. Test for Magnesium.

In testing for magnesium we find an ammoniacal solution of sodic phosphate a most invaluable reagent. The crystals of ammonio-magnesian phosphate have a form so sharply defined and are so characteristic by reason of their hemi-morphism, and the rudimentary crystals have such a particular structure because of this hemi-morphism, that the choice of the salt as a reagent for micro-chemical research will astonish nobody. Numerous experiments have shown me that solid ammonio-sodic hydrophosphate (a salt of phosphorus) gives the most striking results. The drop to be tested, which has already served for the alkali or aluminium tests, is supersaturated with ammonia; at a distance of about 1 c.m. we place a small drop of water, and dissolve a grain of the phosphorus salt in it; communication is then made between the two drops by means of the fine glass rod. In this experiment the distance between the two drops has a preponderating in-

* Abstract of a Paper read before the Royal Society, November 18th, 1886.

* Sulphate of lead separates in the same manner from a solution of sulphuric acid in the form of crossed twins. They are of the same size as sulphate of barium (5 to 12 microns), but the shape of the crystals of strontic sulphate just described, viz., a Maltese cross.

fluence on the formation of well-defined crystals; if the solution contains 1 per cent or more of magnesium, for a considerable time after the liquids are in communication only rudimentary crystals will be formed, of about 60 microns in length at the most; these are badly defined hemimorphs. We only succeed in getting well-defined hemimorphs of about 10 to 20 microns in length in very weak solutions; these crystals, however, are a very long time in appearing if the communication between the drops is too long or too narrow. In such a case we can accelerate the action by making another streak with the glass rod at the side of the first one. If we know beforehand that the solution to be examined can only contain about 0.5 per cent at the most of magnesium, we can simplify the manipulation considerably by placing a small particle of the phosphorus salt, about 0.3 m.grm., on the edge of the drop.

Iron and manganese, which form analogous compounds to that of magnesium, can give rise to no mistakes if, after having added ammonia, we let it settle for a few minutes (the time which is necessary for the complete oxidation of ferrous and manganous salts) before commencing the operation with the ammonio-sodic phosphate.

Sometimes we cannot see the ammonio-magnesian phosphate, or we only get faint indications of it; the reason of this is that there are no ammoniac salts in the solution; it is for this reason that I always recommend the addition of a little hydrochloric acid or chloride of ammonia to the liquid before supersaturating with ammonia.*

The sensitiveness of the reaction is very satisfactory; a solution containing 0.15 per cent of magnesia forms an abundance of crystals in the space of eight minutes; 0.001 m.g. of magnesia can also be found without much trouble.

13. Test for Aluminium.

I found it as difficult to find a reagent for aluminium as it was to find a method of indicating the presence of sodium. But in this instance my efforts have been crowned with a success more complete and still more important, inasmuch as the only blowpipe test for aluminium, that with cobaltic nitrate, permits, as a rule, of a very limited application, and loses still more of its utility when it is necessary to have recourse to the microscope. A reagent which is admirably fitted for the indication of the presence of aluminium, but which is better adapted for use with polished surfaces than with solutions, is an alcoholic solution of alizarin. We allow this liquid to react on a solution of aluminium in an alkali, and we then saturate the excess of alkali with the vapour of acetic acid. In this experiment it is much more convenient to use a strip of filter-paper than a glass plate as a support.

For the examination of prepared solutions I have found chloride of caesium to be an excellent reagent, of which a drop is placed at the edge of the drop to be tested. It suffices to touch the surface of the liquid with the end of platinum wire carrying a small quantity of this salt, to see immediately all round the spot touched the appearance of large crystals of caesium alum, having a diameter of about 35 to 90 microns, and showing the ordinary form; viz., the octahedra, or, more rarely, the combination of the octahedron and the cube. In solutions, no matter how weak, the formation of dendritic masses instead of isolated crystals, is preponderant; when we see them appear it is necessary to add a small quantity of water on exactly the opposite side to that where the reagent was placed. I cannot recommend dissolving the dendrites by heat, because we then obtain, on cooling, much smaller and a less number of crystals than by local precipitation at the ordinary temperature. It is also necessary to prevent a great excess of sulphuric acid. In slightly

acidulated solutions the alum crystals form much quicker, and take a much better shape than in a neutral solution; and further, a slight excess of sulphuric acid favours the solution of aluminic sulphate, which is only slowly dissolved by pure water; a large excess of acid, on the contrary, interferes with and retards the formation of the alum. If any doubts cross our mind as to whether or not we have made any mistake of this kind, we can remedy it by adding an acetate such as that of sodium or of copper.

The presence of iron, even in large quantity, gives rise to no difficulty, since iron alum does not crystallise easily. In some cases, where I have thought the formation of this body possible, I have made controlling experiments with a drop of the same liquid, but in which the ferric salt has previously been reduced by zinc, without, however, arriving at discordant results.

The sensitiveness of the reaction rests on the very slight solubility of caesium alum, of which a large part of the mass consists of water; in fact, to dissolve one part of alum we must have 200 parts of water. One hundredth of 1 m.g. is more than sufficient for a distinct reaction, provided that the solution is reasonably concentrated.

(To be continued).

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 269.)

UPON the conclusion of the reading of the committee's report the President called for the presentation of papers upon the subject.

In response Mr. CLIFFORD RICHARDSON read the following:—

On the Proper Indicator for Detection of Neutrality in Ammonium Citrate Solution for P₂O₅ Determinations.

I have been led to suspect that the cause of some of the discrepancies between analysts in the determination of citrate soluble phosphoric acid lay, at least in a minor degree, in the character of the citrate solution.

The specific gravity is, for instance, to be 1.09, but no temperature is given. Between winter and summer temperatures this might be of some importance.

Neutrality, however, is the point which I think is difficult of obtaining with certainty and uniformity by all chemists.

The question of indicators has been much discussed during the past year, and the principal references I have collected as an appendix to this paper.

The results obtained by the investigators referred to have led me to examine especially the relation of various indicators to citric acid and ammonia.

Solutions were prepared of standard strength, fifth normal, of citric acid and ammonia, and observations made of how closely the various reagents indicated neutrality.

The results, together with a comparison of the use of soda in place of ammonia, and oxalic acid in place of citric, are presented in the accompanying table. (See next page).

With coralline in a saturated alcoholic solution, five drops used in titration gave a sharp change from yellow to pink.

With citric acid and ammonia the indication was less marked than with soda, but easily distinguished.

Thomsen says he found rosolic acid, the colouring matter of coralline, incompatible with ammonia and citric acid. This is not entirely true, and coralline may be depended on for such indications as it furnishes with enough distinctness to read.

* Reciprocally this reaction may serve to indicate the presence of ammonia in a solution. We add sodic phosphate and potash or soda until the reaction is alkaline; then we add a little kieserite. If ammonia is present we see, besides the flocculent precipitate of magnesia, the hemimorphic crystals above described. Nessler's solution only gives a yellow flocculent precipitate.

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

Experiments with Indicators.

Acid, N/5.	C.c. taken.	Alkali, N/5.	C.c. taken.	Indicator.	Remarks.
Oxalic	10.0	Soda	10.05	Coralline	Sharp.
	10.0	"	10.05	"	"
	10.0	Ammonia	10.0	"	"
	10.0	"	9.9	"	"
Citric	10.0	Soda	10.1	"	Not as sharp.
	10.0	"	10.0+	"	"
	10.0	Ammonia	10.0	"	Less sharp.
	10.0	"	9.9	"	"
Oxalic	10.0	Soda	10.05	Lacmoid	End not sharp.
	10.0	"	10.1	"	"
	10.0	Ammonia	9.95	"	"
	10.0	"	9.9	"	"
Citric	10.0	Soda	9.9	"	Indistinct.
	10.0	"	10.3	"	"
	10.0	Ammonia	10.0?	"	Uncertain.
	10.0	"	—	"	"
Oxalic	10.0	Soda	10.7	Poirrier's blue	Not sharp.
	10.0	"	10.8	"	Indistinct.
	10.0	Ammonia	12.3	"	"
	10.0	"	(?)	"	"
Citric	10.0	Soda	10.7	"	Not sharp.
	10.0	"	10.7	"	"
	10.0	Ammonia	11.8	"	Indistinct.
	10.0	"	14.0	"	"
Oxalic	10.0	Soda	10.5	Methyl orange	Sharp.
	10.0	"	10.6	"	"
	10.0	Ammonia	—	"	Not changed.
	10.0	"	—	"	"
Citric	10.0	Soda	10.6	"	Sharp.
	10.0	Ammonia	—	"	Not changed.
Oxalic	10.0	Soda	9.6	Cochineal	Sharp.
	10.0	Ammonia	9.6	"	Less sharp, but distinct.
Citric	10.0	Soda	7.0	"	"
	10.0	Ammonia	6.3	"	"
Oxalic	20.0	Soda	10.1	Phenolphthalein	Sharp.
	10.0	Ammonia	10.1	"	Not so sharp.
Citric	10.0	Soda	10.3	"	Sharp.
	10.0	Ammonia	10.6	"	Not sharp.
Oxalic	10.0	Soda	20.0	Litmus paper	Sharp but changes.
	10.0	"	10.05	"	Reddens on drying.
	10.0	Ammonia	10.0	"	Paper in liquid.
	10.0	"	10.2	"	Drop method.
Citric	10.0	Soda	10.3	"	"
	10.0	"	10.0	"	Paper in liquid.
	10.0	Ammonia	10.0	"	"
	10.0	"	10.3	"	Drop method.
Oxalic	10.0	Soda	10.0	"	Paper in liquid.

With lacmoid the change from red-brown in acid solution is gradual to a violet tint, but is easily followed to a standard colour, except with ammonia, where the change is too gradual.

Poirrier's blue C 4 B in a similar way is easily followed, except with ammonia, from blue to a reddish tinge.

Methyl orange, as described by others, could not, apparently, be obtained in this country. That used was marked Poirrier's Orange No. 3, and was from four sources. It was turned from yellow to red-brown by soda, giving a distinct indication, but was not affected by ammonia. The point indicated with oxalic and citric acids and soda was not, however, neutrality.

Cochineal, in experienced hands, is a fine indicator, but requires a practised eye, and is of no value with organic acids and ammonia for determinations of absolute neutrality.

Phenolphthalein is excluded from consideration by its behaviour with ammonia.

Litmus-paper, as usually prepared, is not reliable. When made by the directions of Sutton* it is very sensitive,

and when immersed in the liquid to be tested gives valuable indication. If a drop of citrate of ammonia is allowed to evaporate on the paper it is reddened, however, so that this method of testing cannot be employed.

Several other indicators have been mentioned frequently of late, such as phenacetolin and gallein. These it was not in my power to investigate.

From the results I was led to conclude that coralline and litmus-paper, carefully prepared by the method given by Sutton and immersed in the citrate solution, are the only indicators available for determining neutrality of citrate of ammonia, with a decided preference for coralline. Litmus is not as delicate, and when used by the drop method in the air is quite unreliable.

I would recommend that coralline be prescribed by the Committee as the required indicator, and that the specific gravity of the citrate be determined at 20 ° C.

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* Francis Sutton, "Systematic Handbook of Volumetric Analysis," Fourth Edition. London: Churchill, 1882, pp. 30-31.

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(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 27th, 1886.

Prof. W. G. ADAMS in the chair.

THE following papers were read:—

"On a Method of Measuring the Coefficient of Mutual Induction of Two Coils." By Prof. G. CAREY FOSTER, F.R.S.

The two coils are, for convenience, designated by P and S (primary and secondary). The method, as originally devised, consists of two parts:—(1). Observing the swing of the needle of a galvanometer placed in

series with the secondary coil, when a current of strength, γ , is started in the primary. (2). Placing the galvanometer and a condenser of known capacity, C, as a shunt between the two points A and B of the primary circuit, such that the first swing of the galvanometer needle, on completing the primary, is the same as in (1). It is easily seen that under these conditions $M = C r r_1$, where M is the coefficient to be determined; r = resistance between the points A and B; and r_1 = resistance of galvanometer and secondary coil. The method requires the value of γ to be the same in the two experiments, and facilities for varying r without altering γ . To overcome these difficulties the arrangement has been modified so as to make it a null method. The connections remain the same as in (2), excepting that the ends of the secondary coil are connected to the terminals of the galvanometer through a variable resistance with no self induction. If p be the resistance of the secondary coil, and variable resistance when adjusted so that on completing the primary circuit the integral current through the galvanometer is zero, it is shown that $M = C p r$ where C and r have the same meaning as before. For let A and E be the potentials of the galvanometer terminals at any time t , γ the resistance of galvanometer, q the current through it, and N and L the coefficients of self induction of the galvanometer and secondary coil respectively. Then, considering the path from A to E through the secondary coil, we have—

$$A - E = p x + t \frac{dx}{dt} - M \frac{dy}{dt}.$$

For path through galvanometer—

$$A - E = q \gamma + N \frac{dy}{dt}.$$

Equating these, and integrating from $t=0$ to $t=\infty$, we get

$$p \int_0^\infty x dt - M \gamma = 0.$$

Since $\int_0^\infty x dt$ = charge of condenser,

$$= C \gamma r,$$

we see that $M = C p r$.

It is easily shown that if $L=M$, then $A-E=0$ for all values of t . Hence the galvanometer might in this case be replaced by a telephone.

By inversion the method could be used for determining the capacity of condensers in absolute measure if M be known. The author thinks the method will be useful for dynamo machines, and gave a series of numbers obtained by experiments on different coils, showing that it gives consistent results.

Mr. C. V. BOYS suggested that by arranging a switch to change the connections from (1) to (2) in rapid succession a steady deflection might be obtained, and thought that this would enable very small coefficients to be determined.

Remarks by Prof. FORBES, Prof. ADAMS, and Prof. PERRY were answered by Prof. FOSTER and Dr. FISON.

"On the Critical Mean Curvature of Liquid Surfaces of Revolution." By Prof. A. W. RÜCKER, M.A., F.R.S.

The paper is chiefly mathematical, and deals with liquid surfaces of revolution attached to two circular rings, the planes of which are at right angles to the line joining their centres. By "mean curvature" the author designates half the sum of the reciprocals of the two principal radii of curvature of the surfaces.

Maxwell has shown, in his article on Capillary Action ("Enc. Britt."), that if the film be a cylinder a slight bulge will cause an increase or decrease in the mean curvature, according as the length is $<$ or $>$ $\frac{\pi}{2}$ times

the diameter. If—

$$l = \frac{\pi}{2} d,$$

then a small change in the volume of the surface will modify its form, but will not alter the mean curvature. Thus the mean curvature of such a cylinder is evidently a maximum or minimum with respect to that of other surfaces of constant mean curvature, which pass through the same two rings at the same distance apart, and which differ but little from the cylindrical form. Hence the cylinder may be said to have a *critical mean curvature* when the distance between the rings is $\frac{\pi}{2}$ times their

diameter. If the distance between the rings is altered a similar property is possessed by some other surface. The author's paper investigates the general relation between the magnitude and distance apart of the rings, and the form of the surfaces of critical curvature.

If x is the axis of revolution, then the equation to a liquid surface of revolution is given by the expressions $x = \alpha E + \beta F$, $y^2 = \alpha^2 \cos^2 \phi + \beta^2 \sin^2 \phi$, where F and E are elliptic integrals of the first and second kinds respectively, of which the amplitude is ϕ and the modulus—

$$K = \sqrt{\alpha^2 - \beta^2} / \alpha.$$

As usual—

$$\Delta = \sqrt{1 - K^2 \sin^2 \phi},$$

whence $y = \alpha \Delta$; and if $K = \sin \theta$, then $\beta = \alpha \cos \theta$; and since $\alpha > \beta$, α and β are the maximum and minimum ordinates.

The results show that as θ increases from 0° to 90° the surface of critical mean curvature is an unduloid, with limits of cylinder and sphere, when $\theta = 0^\circ$ and $\theta = 90^\circ$ respectively. When θ passes from 90° to 180° the surface is a nodoid, with limits of sphere and a circle whose plane is perpendicular to the surface of revolution. In the third quadrant the surface is still a nodoid, the limits of which are a circle and the catenoid. Finally, in the fourth quadrant the surface is an unduloid, the limits being the catenoid and cylinder. Experiments were shown proving that with cylindrical films where $l < \frac{\pi}{2} d$, increase of internal

pressure produced a bulging, whereas if $l > \frac{\pi}{2} d$ a bulging was produced by decrease of pressure. From this it is evident that if the interiors of two cylindrical films whose $l < \frac{\pi}{2} d$ be connected, stable equilibrium will result, whereas if $l > \frac{\pi}{2} d$ there will be unstable equilibrium. These facts were illustrated experimentally with great success.

After some remarks by Mr. C. V. Boys the proceedings terminated.

PHILOSOPHICAL SOCIETY OF GLASGOW. CHEMICAL SECTION.

Friday, November 26th, 1886.

Mr. J. J. COLEMAN, F.I.C., F.C.S., President, in the chair.

Mr. G. G. Henderson, M.A., B.Sc., was elected Vice-President and Mr. John Tatlock Secretary.

It was announced that the "Graham Gold Medal" would be awarded at the end of 1887 for the best paper upon pure or applied chemistry communicated and read to the Society during the three sessions ending April, 1887, and that papers would still be received, but should be sent early so as to receive proper consideration. The authors of papers need not necessarily be members of the Society.

Neutralisation-Heat of Homologous or Isomeric Monobasic Acids.—H. Gal and E. Werner have determined these heats for the isobutyric, trimethylacetic, caproic, and isobutylacetic acids.—*Comptes Rendus*.

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. Vol. II.—Fixed Oils and Fats, Hydrocarbons, and Phenols. By A. H. ALLEN, F.I.C., F.C.S., &c. Second Edition, revised and enlarged. London: J. and A. Churchill.

THIS volume has long been looked for, and now it has appeared it will, we think, be received with very general satisfaction. The author, as all readers of the foregoing volume and of the former edition will be aware, has proceeded on a system the direct reverse of that adopted, e.g., in Dr. Normandy's "Commercial Handbook of Chemical Analysis." He does not give in alphabetical or other order the various organic articles of commerce, the intermediate products, raw materials, and residues, but he gives what may be called a systematic classification of organic products, giving of course prominence to those which are chiefly used in the arts. Thus the three main divisions of this volume are—Fixed Oils and Fats, Hydrocarbons, and Phenols.

The aromatic acids and tannin, also the colouring-matters, cyanogen compounds, organic bases, albumenoids, &c., are announced as to follow in the third volume. It is not easy to pronounce whether, of the two arrangements, that of Mr. Allen or that of Normandy and others should be preferred.

For the determination of the fatty matters in milk the author gives a process, devised by Mr. A. Adams, and formally recommended by a Committee of the Society of Public Analysts. For the details of this method we must refer to the work itself.

The examination of oils is discussed at considerable length, the physical properties and chemical reactions by which they are distinguished being described in a very elaborate manner. There are Tables of the specific gravities of oils, taken both at 15.5° and at 98° — 99° , as recommended by Estcourt. At the latter temperature the observation is preferably made with a Sprengel tube, or, if the quantity of the sample is sufficient, with a Westphal balance. A further Table gives a very comprehensive classification of the oils, with their respective classification equivalents. The author thinks it probable that linoleic acid has a higher molecular weight than that commonly assigned to it.

Considerable attention has been paid to the recognition of the presence of hydrocarbons in fixed oils, an addition which is now frequently made both for legitimate and for fraudulent purposes.

Under "Cotton-seed Oil" he remarks that its principal applications are in soap-making and in the manufacture of factitious butter. For this purpose we should consider it decidedly preferable to any animal fat, as there is no possibility of the introduction of disease germs.

The process described in a footnote, as followed in the preparation of cod-liver oil, is scarcely on a level with the practice of the present day.

The two kinds of Turkey-red oils—the old emulsive oil, or *huile tournante*, and the more recently discovered "alizerine oil" obtained from castor oil—are clearly distinguished, and satisfactory methods for their examination are laid down. This is a point of some value, since these two oils are occasionally confounded, and since alizerine oils occur in the market which are of very inferior value.

The statement of Wanklyn and Fox, that manufacturers never obtain more than 5 per cent of glycerin on saponifying fats, is shown to be at issue with experience, as some manufacturers actually recover from $7\frac{1}{2}$ to 8 per cent, although a not inconsiderable quantity is lost during

concentration. The theory of an iso-glycerin, propounded by the same chemists, is pronounced to be ingenious but unsupported by evidence.

The account of the behaviour of soaps, of the additions to which they are liable, and of the methods to be followed in their examination, is thorough-going, and will be found most useful. We find the remark that saponification in the so-called cold process is very incomplete. This is perfectly true in the case of soda-soaps, which the author has in view, but with potash the result is much more satisfactory. The addition of cane-sugar to soaps is justly condemned as a mere dilution. The value of glycerin, over and above the proportion formed during saponification, is duly recognised. We note as a curiosity that a certain advertised soap, the alleged curative properties of which are ascribed to an admixture of milk and sulphur, contains neither of these bodies, but instead "a large admixture of china clay and a most objectionable proportion of free alkali."

There is an outline general scheme for the analysis of soaps, which of course every analyst will somewhat modify according to circumstances.

It is recommended that manufacturers' soaps should be tested for the proportions of water, total alkali, and crude fatty acids; while the percentages of caustic alkali, alkali as carbonate and silicate, combined fatty and resin acids, and free fatty acids and unsaponified oil, are secondary determinations which are frequently of considerable importance.

The second chapter of the volume is devoted to the hydrocarbons, and passes in review a truly vast number of products, some of them of extreme importance. Separate sections treat of the tabular arrangement of hydrocarbons in series; destructive distillation and its products; the tars, bitumens, petroleum, and shale-products; the terpenes and their allies; benzene and its homologues; naphthalene and its derivatives; and, lastly, the anthracene group. Mr. Allen draws here a very useful distinction between benzene, the definite chemical individual, and benzol, the commercial mixture of benzene with some of the homologues and with certain impurities. We recommend this distinction for general adoption, since there prevails at present a most annoying confusion between benzene, benzol, benzine, and benzoline, terms sometimes used as synonyms and sometimes applied to distinct bodies. A similarly useful distinction is here drawn between nitrobenzene and nitrobenzol, toluene or toluol, &c.

The last chapter, which space does not allow us to examine, deals with the phenols.

This volume, like its predecessor, will doubtless be very generally appreciated by chemists. The index might with advantage have been more copious.

The Swelling Power of the Sulphocyanides, and Tumefaction as the Cause of Fermentative Reactions. (Die Quellkraft der Rhodanate, und die Quellung als Ursache fermentartiger Reaktionen.) By Dr. EDUARD MEUSEL. Gera: A. Reisewitz.

THE author of this work entered upon his investigations with a view to ascertain the reason why sulphocyanides exert a destructive action upon vegetation. Comparative experiments made upon peas, beans, grains of wheat, rape-seed, and linseed, with ordinary water and with solutions of the sulphocyanides, showed that no germination took place in presence of the latter, even in such small quantities as $\frac{1}{2}$ per cent. The seeds moistened with these solutions swell up more quickly and rapidly than those soaked with pure water. Further, whilst in the latter case the cotyledons remain almost dull, those in contact with a sulphocyanide solution became almost transparent at the margin and decidedly translucent even in the middle. The sulphocyanide solutions appeared to have exerted a solvent power, withdrawing from the seeds

starch, calcium phosphate, and in the case of wheat gluten, and albumenoids in the other seeds. The injurious action of sulphocyanides upon vegetation is due especially to their specific power of producing abnormal swelling.

Solutions of sulphocyanides, at from 15 to 20 per cent, convert starch at once into paste at ordinary temperatures. The presence of other salts retards this action, with the exception of common salt and of calcium chloride. A 30 per cent of this latter salt alone converts starch gradually into paste at the common temperature. Stronger solutions do not effect this reaction.

As regards the action of the sulphocyanides upon vegetable albumenoids, the author has observed that the albumen of the carrot and the legumine of beans are both coagulated by the sulphocyanides in the shape of fine flocks. The gluten of cereals swells up strongly, and dissolves in liquids containing sulphocyanides and is reprecipitated by phosphoric acid.

The effects of sulphocyanides upon egg-albumen may be shown as follows:—8 parts of potassium sulphocyanide are rapidly dissolved in 30 parts white of egg, and filtered. In about two days the filtrate congeals, at common temperatures, to a white gelatinous mass, from which water extracts no soluble albumen. If the white of egg is first acidified with phosphoric acid, an addition of sulphocyanide produces at once a white precipitate of coagulated albumen.

The serum of blood, mixed with 5, 10, or 15 per cent of ammonium sulphocyanide, has a very slight acid reaction, and if left to itself, at ordinary temperatures, for a day it becomes a transparent jelly, which on treatment with water yields white insoluble albumen, whilst the filtrate still holds albumen in solution. If serum is very faintly acidulated with hydrochloric acid, and a very small quantity of a sulphocyanide is further added, it coagulates about the temperature of the blood, a circumstance which may be pathologically important.

Hides previously freed from hair and immersed in solutions of a sulphocyanide, swell up to nearly five times their former thickness, and become remarkably elastic. If the solution is weak, the hide on drying will lose this elasticity, but if it contains from 20 to 24 per cent of the solid salt the mass on drying becomes perfectly equal to caoutchouc in elasticity. Animal membranes which have been swelled by soaking in a sulphocyanide allow animal albumen, which is otherwise of a colloidal nature, to diffuse through them. The author is of opinion that the presence of albumen in urine is proof of an abnormal swelling of the membranes or membranous tissues.

For the detection of albumen in cases where the necessary reactions of nitric acid might prove objectionable, the author recommends to acidify strongly with phosphoric acid, and then to precipitate the albumen with ammonium or potassium sulphocyanide.

The sulphocyanogen present in the saliva he considers as having the function of keeping the mucous membranes moist and elastic, and of aiding in the saccharification of starch.

In an especial section, in which there occurs no mention of the sulphocyanides, Dr. Meusel explains the intense and rapid action of the nitrates as top-dressings by their power of accelerating saccharification. On the contrary, carbolic and salicylic acids check the saccharification of starch.

In a final section the author infers that almost every substance is capable of saccharifying starch in proportion to its power of enveloping water.

Manual of Assaying Gold, Silver, Copper, and Lead Ores. By WALTER LEE BROWN, B.Sc. Second Edition, thoroughly revised, corrected, and augmented. Chicago: Sargent and Co.

In the Preface the author expresses his conviction that there is no book in the language on the subject occupying

the place which his work seeks to fill. Some such publications he considers antiquated, whilst others fail to supply the necessary details or are more suitable as works of reference. Omission of complete working instructions is a fault which certainly cannot be laid to Mr. Brown's charge; he describes every appliance and every process in a very clear, thorough-going, painstaking style.

In the Introduction we find a praiseworthy attempt to draw a clear distinction between *assaying* and *analysis*. The former art he defines as the method of finding out "of what a substance is composed, and the proportions by means of *dry* reagents and *heat*," whilst analysis reaches the same end by the use of *wet* reagents with or without heat. Mr. Brown is of course aware that his distinction, though very convenient, is not the only one which has been proposed. Thus some writers insist that the task of the analyst is the detection and determination of every substance present in a compound or mixture, whilst the assayer seeks merely to determine some one constituent upon which the commercial value of the sample chiefly depends; whilst others, again, call every determination effected for the purposes of manufacture or trade an assay.

In the first part of the work the author describes the apparatus and reagents required by the assayer. He sets out with the appliances for comminution, figuring and describing the crushing-mills of Lipy, Krom, and Bosworth, which, when the work to be done is abundant or the samples bulky, should be driven by power. The Richards pulveriser, or "arresta," is recommended for the amalgamation of small quantities of ores.

The subject of scales and balances is introduced at some length, and the instructions for manipulating these delicate appliances are satisfactory. Among balances the palm is awarded to one of Oertling, though that by Ainsworth is pronounced "a recent but worthy rival to the Oertling." It is said to be sensitive to 1-100th milligramme.

Among furnaces the first place is given to those employing gaseous fuel, where such is to be had. Some of those figured and recommended, such as the "Monitor," are modifications or adaptations of Fletcher furnaces.

Hoskins's "hydrocarbon assay-furnace," burning refined petroleum or gasoline, receives also a very good character.

Under the head "Reagents" we notice a useful Table of the reducing power of different forms of carbons, carbohydrates, &c.

The careful testing of reagents before putting them in actual use is insisted on. The author, while giving a suitable method for determining silver and lead, points out that litharge absolutely free from silver cannot be met, and that if it could the advantage would be very doubtful.

In Part II. the author formally describes the most approved process for assaying ores of gold, silver, copper, and lead. He mentions that the colours shown by the interiors of scorifiers are often characteristic of the ores tested, and in conjunction with the colours of the cupels make valuable test. The colours thus produced in the respective presence of copper, iron, lead, manganese, chrome, and uranium, are shown in a coloured plate.

The chapter on the dry assays of copper ores is brief, the author fully recognising their want of accuracy.

The Appendix contains, among other valuable matter, a description of Luckow's electrolytic analysis of copper ores; of the volumetric method for the same ores with potassium cyanide in an ammoniacal solution, instructions being given for eliminating interfering metals, such as zinc, nickel, and cobalt; the pan-test for gold; the chlorination assay of gold ores; qualitative tests for metals, and for the acids accompanying them in ores; and determination of sulphur in pyrites, for which he recommends treatment with potassium chlorate and nitric acid.

The Appendix further contains lists of the minerals

occurring in the United States known to contain gold, silver, copper, or lead; a catalogue of books on subjects more or less connected with assaying; a plan showing the arrangement of an assay laboratory; together with a variety of Tables. The Index is fairly copious.

The work is, of course, mainly drawn up with an eye to American affairs, but we believe that it will be found useful in all countries where the English language is spoken.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 20, November 15, 1886.

Researches on the Phosphates.—M. Berthelot.—The insoluble alkaline-earthly phosphates obtained by double decomposition with tribasic sodium phosphate are capable of several distinct conditions, the one colloidal, gelatinous, containing a large proportion of water retained by the salt, properly so-called; the other crystalline, containing also combined water, but in a smaller proportion. The formation of the colloidal salt is accompanied by an absorption of heat, followed by a very considerable disengagement, which answers at once to the crystallisation and to the changes which take place in the state of combination of the acid with the base, and of the resulting salt with water.

Velocity of Dissociation.—H. Lescœur.—The considerations drawn from the velocity of dissociation yield valuable information as to the existence of hydrates and analogous compounds; but they can throw no light, either absolutely or relatively, on the value of the tensions of dissociation. The velocity of dissociation, in fact, is not merely a function of the tension of dissociation, but it depends also on the physical condition of the bodies, an element which eludes all measurement.

Certain Laws of Chemical Combination.—MM. de Landero and R. Prieto.—The authors consider chemical combination as being produced by a shock between the particles of the element forming a compound. They suppose that the particles of each element are in motion with a certain speed, and that such speed is a constant characteristic of each body. The loss of energy or of *viv* due to the shock between the non-elastic particles is considered as the equivalent of the quantity of heat liberated by the combination.

Journal für Praktische Chemie.

New Series, Vol. xxxiv., Parts 6 and 7.

Picolic and Nicotinic Acid.—Eugen Seyfferth.—The author describes the behaviour of picolic acid with fuming hydriodic acid, with zinc powder and glacial acetic acid, and with phosphorus pentachloride. He then discusses the reactions of nicotinic acid with phosphorus pentachloride.

On the Transferrers of the Halogens.—C. Willgerodt.—There are addition- and substitution-transferrers. Among the former are aluminium hydroxide and alum. They must, above all things, possess the property of not effecting the substitution of hydrogen by the halogens, since addition disappears where substitution occurs. It seems to the author that no substance can be at once an additive and a substitutive transferer. The additive transfer of the bodies mentioned seems to depend not upon chemical, but upon purely mechanical processes, and is mediated by their relation to light. No elements capable

of forming only a mono-, a mono- and di-, or only a di-haloid are substitutive transferers. Some, though not all, elements which form tri-, tetra-, or penta-haloids, are transferers, the efficacy of a body in this respect depending not merely on its grade of halogenation, but upon the movability of the halogen atoms in the compound. This latter property again is, in part at least, a function of the chemical affinity of the inorganic haloid and of the organic substance. If the transferring elements are arranged according to the natural groups of the periodic system we find that the haloids of the elements of the first group are not transferers. Gold is an exception; this element belongs to the natural group of aluminium and thallium. If we leave it in the first group we see that this mono- and trivalent element has the highest atomic weight in the group, and we are thus led to the idea that the transferring power of an element of a group is connected with the atomic weight. The elements of the second group are not transferers. In the third group boron, with the lowest atomic weight, seems not to transfer; thallium, the final element of this group, is a brilliant transferer. In the fourth group carbon and silicon are doubtful; tin is very efficient; lead does not transfer, as PbCl_4 is not formed under the circumstances. In the fifth group nitrogen, phosphorus, and arsenic have no action; antimony is very powerful; bismuth less so, since, though its atomic weight is higher, it forms only a tri-compound, in which the halogen is less movable than in the corresponding penta-compound. In the sixth group sulphur is the first transference element, tellurium is much more energetic, as is also molybdenum. In the seventh group iodine is a powerful transferring agent, and in the eighth, iron.

Weight of Drops, their Relation to the Constants of Capillarity, and the Capillary Marginal Angle.—J. Traube.—In this interesting investigation, the completion of which has yet to follow, the author proposes the following law:—"The volumes of drops are proportional to the height at which the liquids stand in capillary tubes, or, the weights of the drops are proportional to the products of the capillary ascent into the specific gravity."

Calorimetric Researches.—F. Stohmann.—In his ninth and tenth memoirs, here included, the author discusses the thermic value of the homologues of phenol, and the thermic value of the methyl groups in homologous phenols.

Ultramarine Blue in the Moist Way.—F. Knapp.—The author describes the production of ultramarine blue in the moist way from a variety of mixtures in which all the constituents of ordinary ultramarine are not present. Common salt may be permanently tinged blue with sulphur alone.

Production of Substituted Stilbenes from Substituted Halogen Benzyles.—K. Ebs.—The author obtains a para-brom-benzoic ethylester, a colourless mobile liquid, heavier than water, soluble in the ordinary solvents except water, boiling at 236° under the pressure of 713 m.m., and being saponifiable only with great difficulty.

On Substituted Stilbenes.—K. Ebs and F. Bauer.—In this first communication the authors treat of para-dinitro-stilbene.

The Derivatives of Taurine.—J. W. James.—Here the author describes the decomposition of trimethyl-aurine with bases, and its behaviour with cyanamide and hydriodic acid.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. 4th Série. Vol. i., No. 8, August, 1886.

The Solubility of Antimony Oxide in an Alkaline Solution of Glycerin. A New Mordant for Cotton-Dyeing.—Dr. H. Kohler.—The author proposes to dissolve antimony oxide in an alkaline solution of glycerin and to use the resulting liquid in cotton-dyeing, especially for fixing tannin upon the fibre.

MISCELLANEOUS.

Chemical Scholarship.—We wish to draw the attention of our younger readers to a Scholarship of the value of £50 per annum, tenable for two years, which will be awarded at University College, Liverpool, to Chemical Students, early in December. The Scholarship, which bears the well-known name of Sheridan Muspratt, is not confined to Students of the College. Further particulars will be found in our Advertising Columns.

On Certain Derivatives of Methyl Carbanilate.—W. Hentschel.—By cautiously heating methyl carbanilate with sulphuric acid there is formed a soluble compound which the author at first regarded as sulpho-methyl-amido benzoic acid, but which may, perhaps, be rather regarded as the sulphonic acid and methyl carbanilate.—*Fourn. fur Prakt. Chemie.*

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Official Chemists.—1. How many chemists are employed at Somerset House, and where and how can I get information as to the payment they receive and the manner of their appointment? 2. Are there any appointments open to chemists under the Board of Trade, the Board of Works, the Home Office, Local Government Board, War Office, Admiralty, and Customs? 3. Where can I find information relating to them?—A. B. H. FAUDELLE.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—London Institution, 5.
— Medical, 8.30.
— Society of Arts, 8. (Cantor Lectures). "The Principle and Practice of Ornamental Design," by Lewis Foreman Day.
— Society of Chemical Industry, 8. "On Strontium Hydrate," by E. H. Träschel.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 7th.—Institution of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 8th.—Society of Arts, 8. "Glow Lamps, their Use and Manufacture," by Major-Gen. C. E. Webber.
— Pharmaceutical, 8.
THURSDAY, 9th.—Royal, 4.30.
— London Institution, 6.
— Royal Society Club, 6.30.
— Mathematical, 8.
FRIDAY, 10th.—Astronomica, 8.
— Quekett Club, 8.
SATURDAY, 11th.—Physical, 3. "On the Influence of Change of Condition from the Liquid to the Solid State on Vapour Pressure" and "On the Nature of Liquids as shown by a Study of the Thermal Properties of Stable and Dissociable Bodies," by Prof. W. Ramsay and Dr. Sydney Young. "On Cauchy's Theory of Reflection and Refraction," James Walker.

UNIVERSITY COLLEGE, LIVERPOOL.

SHERIDAN MUSPRATT CHEMICAL SCHOLARSHIP.
Of the value of £50 per annum, tenable for Two Years.

The Examination for this Scholarship will commence on December 9th, the subjects of examination being:—

The Principles of Chemistry.
Chemistry of the Metals and Non-Metals.
Elements of Organic Chemistry.
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The examination in these subjects will extend over three days, one at least of which will be devoted to practical work in the Laboratory. Candidates who have not taken a University Degree will further be required to satisfy the Examiners in—

1. Physics: especially Heat and Electricity.
2. Mathematics; especially Algebra up to Binomial Theorem and Logarithms.

The Examination is open to all, but preference will be given to Candidates under 23 years of age, provided that they come up to the requisite standard.

Candidates should send their names on or before Dec. 6th to
THE REGISTRAR.

THE CHEMICAL NEWS.

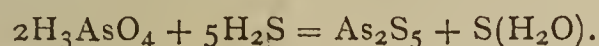
VOL. LIV. No. 1411.

PENTASULPHIDE OF ARSENIC.

(PRELIMINARY NOTICE).

By LEROY W. McCAY, D.Sc.

A SOLUTION of an alkali arseniate strongly acidified with hydrochloric acid and saturated with sulphuretted hydrogen gas is, when heated for *one* hour in a tightly stoppered bottle and in a water-bath, the water of which has been brought to active boiling, completely changed to pentasulphide of arsenic—



The lemon-yellow precipitate is free from any admixture of As_2S_3 . It is chemically pure As_2S_5 , barring the presence of a trifling quantity of sulphur, which is separated from the excess of sulphuretted hydrogen by the action of the air dissolved in the liquid or left in the upper part of the bottle. By boiling the solution prior to passing the sulphuretted hydrogen gas, filling the bottle almost full of freshly boiled water, and then heating for one hour in the boiling water-bath, the amount of sulphur precipitated sinks practically to a vanishing quantity, and the sulphide is obtained in a state which, as said, is to all intents and purposes chemically pure. The pentasulphide thus obtained exhibits the following reactions: (1) Carbon bisulphide extracts from it no sulphur; (2) it is soluble in strong ammonia water without the separation of sulphur; and (3) the ammoniacal solution, when diluted, shaken up with excess of nitrate of silver, and filtered, gives a clear filtrate, from which, upon the careful addition of nitric acid, reddish brown arseniate of silver is precipitated.

This method of precipitating arsenic as the pentasulphide is extremely interesting, and serves to substantiate the results arrived at by Bunsen, who, in 1878, showed that As_2S_5 was indeed formed by the action of sulphuretted hydrogen gas upon arsenic compounds in solution, but only completely thrown down provided the solution of arsenic acid be kept hot, and the gas in large quantities be passed for a very long time.

I have spent much time and labour in endeavouring to clear away the uncertainty which attaches to this subject of the formation of pentasulphide of arsenic by the action of sulphuretted hydrogen upon arsenic acid, and I trust ere long to be able to publish a detailed account of my work. Experiments, test analyses, and so on, I withhold, then, for some time in the near future.

John C. Green School of Science, Princeton, N.J.,
Nov. 10, 1886.

A NEW AND SIMPLE METHOD FOR ESTIMATING FLUORINE, ESPECIALLY APPLICABLE TO COMMERCIAL PHOSPHATES.*

By A. CHAPMAN.

THIS method depends on the fact that acid ammoniac acetate (*i.e.*, ammonia more than neutralised by acetic acid) precipitates calcic fluoride, but not calcic phosphate, from solution in acids.

2.5 grms. are ignited in a platinum crucible for a short time (this ignition prevents ferric and aluminic phosphates from dissolving in dilute hydrochloric acid), transferred

to a mortar, and ground up with repeated small quantities of 10 per cent hydrochloric acid, filtered, and washed.

The filtrate and washings are made up to 250 c.c. 100 c.c. of this are taken and added to the acid ammoniac acetate, the calcic fluoride is precipitated, and calcic phosphate remains in solution.

The calcic fluoride is filtered off, washed, dried, ignited, and weighed as usual.

If the substance be not ignited the calcic fluoride comes down mixed with ferric and aluminic phosphates, from which the amount of calcic fluoride can be obtained by subtracting the amount of ferric and aluminic phosphates.

This second method is not so accurate, as, even without ignition, all the ferric and aluminic phosphates do not dissolve up.

This method was originally devised by Dr. Graham, of the Birkbeck Laboratory, University College.

THE UNITED STATES LABORATORY AT THE NEW YORK PUBLIC STORES.

By MARCUS BENJAMIN, Ph.B., F.C.S.

IN the CHEMICAL NEWS, vol. liii., p. 267, was published a historical sketch of the United States Laboratory, together with an account of the library and two of the three branches of the laboratory department. The remaining branch, a description of which will complete the subject, is under the immediate charge of Jesse P. Battershall, who studied in the Columbia College School of Mines, and subsequently received the degree of Doctor of Natural Philosophy, at the University of Tübingen, Germany, for original investigations in the naphthaline series. Dr. Battershall is assisted by Mr. J. Howard Wainwright, Ph.B., F.C.S., a graduate of the Columbia College School of Mines; Dr. J. Frank Davis, who was graduated at the Bellevue Hospital Medical College; and Mr. Ernest G. Chapman. The laboratory, which is a moderately well equipped one, is the only establishment of its character connected with the United States Customs Service. It contains several scales, including two of Becker's most delicate balances, on which it is possible to weigh one one-hundredth of a milligramme; an excellent assortment of platinum-ware, of which the large evaporating dishes are used in the determinations of ash in the tea assays; a Scheibler's carbonic acid apparatus; well arranged water baths for evaporation, where at times upward of a dozen determinations of morphine are being carried on; blast apparatus; Fletcher's burners; combustion furnaces for organic analysis, and other conveniences too numerous to mention.

The character of the work is, naturally, somewhat varied; it includes assays of tea; of drugs, such as opium, quinine, jalap, and similar substances; analysis of lead, ashes, various alloys, iron and copper ores; determinations of alcohol in wines, spirits, tinctures, and other preparations of drugs; also examinations of glycerin, kainit, and many other qualitative and quantitative estimations for customs purposes.

The unsatisfactory nature of the teas brought into the United States led to the passing of an Act by Congress prohibiting the importation of "any merchandise for sale as tea, adulterated with spurious or exhausted leaves, or which contain so great an admixture of chemicals or other deleterious substances, as to make it unfit for use." In consequence of this Act all teas are now analysed at the U.S. laboratory. Those samples which fail to comply with the requirements cannot be entered in this country, and they are re-shipped and sold elsewhere. During the year 1883 upward of seven hundred examinations of tea were made, and this number has steadily increased since.

The tea assays, which are chiefly made by Dr. Davis, consist of the following determinations:—Total ash, ash

* Read before the Chemical and Phys. cal Society, University College, Dec. 2, 1886.

insoluble in water, ash soluble in water, ash insoluble in acids, extract, insoluble leaf. The method of analysis followed is the one devised by Dr. Battershall, and described by him in his "Legal Chemistry."* The general outline of the processes are as follows:—Total ash—five grms. of the sample are placed in a platinum vessel and heated over a Bunsen burner until complete incineration has been accomplished. The vessel is allowed to cool in a desiccator, and is then weighed as quickly as possible.

Ash Insoluble in Water.—The total ash obtained, as previously mentioned, is washed into a beaker and boiled with water for a considerable time. It is then placed upon a filter, and the insoluble residue washed, dried, ignited, and weighed.

Ash Soluble in Water.—The proportion is obtained by deducting the ash insoluble in water from the total ash. The ash insoluble in water is boiled with dilute hydrochloric acid, and the residue separated by filtration, washed, ignited, and weighed.

The Extract.—Two grms. of the carefully sampled tea are boiled with water until all soluble matter is dissolved, water being added from time to time to prevent the solution becoming too concentrated. The liquid is poured upon a tared filter, and the remaining insoluble leaf repeatedly washed with hot water until the filtered liquid becomes colourless. The filtrate is now diluted to a volume of 200 c.c., and of this 50 c.c. are taken and evaporated in a weighed dish over the steam bath until the weight of the extract remains constant. Its weight is then determined.

Insoluble Leaf.—The insoluble leaf obtained in the preceding operation, together with the weighed filter, is placed in an air-bath and dried for at least eight hours, at a temperature of 110° C. Its weight is then determined.

It should be noted that in the foregoing estimations the tea is taken in the ordinary air-dried condition. If it be desired to reduce the results obtained to a dry basis, an allowance for the moisture present in the sample (an average of eight per cent), or a direct determination of the same must be made.

The opium assays rank next to those of tea in point of number. All of this substance that is brought into the United States must contain at least nine per cent of morphine. Frequently a cargo containing twenty or more samples are received at the appraiser's store. Indeed, during the month of April, 1885, there were 108 estimations of morphine received. Hence, it was necessary to adopt some method which would comply with the following conditions: rapidity of manipulation, simplicity of apparatus, and accuracy of results. Mr. Wainwright undertook the solution of this problem, and after careful study of the different processes in use, adopted that recommended by Dr. E. R. Squibb.† Besides careful sampling, in fact, this is one of the most important details to be considered, the assay consists of three distinct operations: the preparation of the extract, separating the morphine, and treatment of the separated alkaloid.

Preparation of the Extract.—Ten grms. of the sample are introduced into an ordinary six-ounce wide-mouthed bottle, fitted with a good cork. Then 100 c.c. of boiling water are added, the bottle tightly corked, and after frequent hard shaking allowed to stand from twelve to twenty-four hours (generally over night). The extract is then decanted upon a filter, 50 c.c. of hot water is added, the bottle again well shaken, and its contents transferred to the filter. When the liquid ceases to drop the contents of the filter are put back into the bottle, again shaken with 50 c.c. of water, after which it is thrown upon the same filter, and washed until the water comes through colourless. The filtrate is now concentrated over a water

bath to a volume of about 25 c.c. This extract is then transferred, using as little water as possible, into an accurately tared Erlenmeyer flask, provided with a tight cork and allowed to stand.

Separating the Morphine.—After cooling, 10 c.c. of 95 per cent alcohol are added and the flask agitated; then sufficient ether is added, the cork tightly fitted, and the flask again well shaken. After this, and before the ether has had time to separate, about 4 c.c. of a 10 per cent solution of ammonium hydroxide is poured in. The flask is then well shaken until the crystals of morphine begin to separate. It is then set aside in a cool place until the alkaloid has entirely separated (generally over night).

Treatment of the Separated Alkaloid.—When the separation is complete, the upper portion of the ethereal fluid is carefully decanted through a tared filter; then 20 c.c. of ether is poured into the flask, and, after slight agitation, carefully poured on the filter. The paper is washed with more ether, applied drop by drop around the edges. The crystals remaining in the flask are then washed upon the filter with cold water, and the washing continued until the filtrate comes through colourless. The filter and contents are then pressed between folds of blotting-paper and dried in an air-bath at 100° C. The tared flask is likewise dried and weighed if any crystals adhere to its sides. Weighing and calculating results complete the operation.

In the analyses of lead ashes and alloys the usual methods of separation, recommended by Fresenius and others, are used. The copper matte estimations are made by the ordinary electrolytic method. In the case of ores the same process is employed. With iron oxides a simple determination of the oxide is all that is considered necessary. This is accomplished by means of precipitation with ammonium hydroxide and subsequent separation. Under this head may be included various pigments, such as colcothar, crocus martis, Indian red, and similar compounds; also the polishing powders with various names, on which duty is levied according to the amount of iron oxide which they contain.

Examination of substances containing alcohol consists in determining the amount of absolute alcohol by distillation, and then taking the specific gravity of the distillate. The examination of glycerin is somewhat crude, although, in the hands of those who have had experience in the matter, it becomes very easy to determine whether the sample under inspection is raw or refined, as the duty is regulated according to the quality of the glycerin. The assay includes the following tests:—The reaction with litmus-paper; Determining the specific gravity; The examination of the precipitate with silver nitrate, lead acetate, barium chloride, and ammonium oxalate. The determination of the carbonaceous residue and of the mineral ash also are made. The vinegar determinations which are daily made consist in taking the specific gravity of the sample, and in ascertaining the number of grains of potassium bicarbonate required to neutralise one troy ounce of the fluid. Phenolphthalein has been used as an indicator, and gives every satisfaction.

The examination of kainit, potassium sulphate, and manure salts is frequently required on account of the large amounts of these substances imported from Germany. The method* followed consists in dissolving ten grains of the sample in 200 c.c. of water, and, after diluting to 1000 c.c., filtering; 25 c.c. of the filtrate is diluted to 150 c.c., and a slight excess of barium chloride is added; then, without filtering, add barium hydroxide in slight excess. Filter and wash until the precipitate is free of chlorides. To the filtrate add 1 c.c. of strong ammonium hydroxide, and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Add in fine powder 0.5 of a gm. of pure oxalic acid, or 0.75 gm. of ammonium oxalate. Filter, wash, and evaporate the filtrate to dryness. Then ignite until all volatile matter

* "Tea and its Adulterations," p. 134, et seq.

† "Ephemeris," vol. 1, p. 15.

* See "Methods of Analysis of Commercial Fertilisers," Bulletin No. 7, Department of Agriculture, Washington, 1885.

is driven off. The residue is digested with hot water, filtered, and diluted to 30 c.c. To the filtrate two drops of strong hydrochloric acid are added, and then 10 c.c. of a solution of 10 grms. of platinum chloride in 100 c.c. of water. The mixture is evaporated to a thick syrup over a water bath, treated with 85 per cent alcohol, well rubbed with the stirring rod, washed with 85 per cent alcohol by decantation, collected on a filter, again washed with alcohol, dried, and weighed.

In addition to the foregoing, the chemist is called upon to determine numerous compounds, which have been entered under the names of "chemical salts," "medicinal preparations," "acid bases," "no name," and similar titles. A curious illustration of the latter occurred in an undesignated compound, which was apparently a mixture of chalk and some organic body. The determination of the character of the latter for some time baffled the examiner, until, after tasting it, the numbness produced on his tongue suggested cocaine, a theory which was subsequently corroborated by the proper tests.

Questions of the gravest importance, involving thousands of dollars of duty, are often referred to the laboratory for decision. The opinion given is sometimes questioned, and its correctness must be defended in open court. This requires considerable research on the part of the chemist, as well as a high degree of competency. During recent years the most notable of these cases was a series involving the correctness of the chemist's report of the analysis of colcothar, and later several questioning the accuracy of his results in analyses of bone-black. Frequently subjects dealing with chemical technicalities are referred to the chemist for consideration. Of this nature was the important decision which turned on the question as to whether Apollinaris water was natural or artificial. These questions, though usually of less prominence than that previously referred to, are sent to New York from every port of entry in the United States; and, according to the report received, the amount of duty to be levied is fixed. From the description thus given of the work accomplished by Dr. Battershall and his assistants, some idea of the scope and magnitude of the United States Laboratory may be obtained.

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 280.)

14. Test for Iron and Manganese.

It does not appear to me to be necessary to use the microscope in testing for iron, inasmuch as the colour of the fine precipitate caused by ferrocyanide of potassium in solutions of ferric salt is quite as easily detected with the naked eye as it is under a magnifying power of two hundred times.

The test for manganese, which is based on the formation of a manganate by fusion with sodic carbonate exposed to the air, offers a means so certain and so characteristic for detecting traces of this metal that a microscopic test is quite superfluous.

15. Test for Metalloids.

The tests for some of the metalloids can be made by inverting some of the reactions already described (sulphur according to § 13; and phosphorus according to § 12). I have been compelled to devise special tests for the detection of chlorine, fluorine, boron, and silicon.

16. Test for Sulphur.

In testing for sulphur it is first of all necessary to transform it into a soluble alkaline sulphate. In cases where we have to deal with sulphides and sulpharsenates, we

must oxidise them by fusing them with equal parts of carbonate of soda and nitre; the insoluble sulphates are melted with pure alkaline carbonate.

The resulting mass is broken up into a coarse powder: this is moistened with a drop of water, and a drop of a mixture of chloride of aluminium and hydrochloric acid is then added, with a little chloride of caesium. We then proceed as has been previously indicated (§ 13), and we find the first crystals of caesium alum close to the glass rod.

17. Test for Phosphorus (and Arsenic).

The insoluble phosphates are treated in exactly the same manner at first as the insoluble sulphates. As a reagent we use a concentrated solution of chloride of ammonium and a grain of crystallised sulphate of magnesia (or better still kieserite, as it dissolves more slowly), and after that we proceed in the manner just now referred to in § 12.

The manner of preparation is the same for arsenides as it is for sulphides; that which serves to transform insoluble sulphates into alkaline sulphates, which of course are soluble, applies equally to insoluble arseniates. The microscopic crystals and the general crystalline character of ammonio-magnesian arseniate resemble, and may even be mistaken for, those of the corresponding phosphate. Experiments undertaken with the idea of obtaining a characteristic colouration on the surface of the crystals of the arseniate by means of sulphuretted hydrogen and nitrate of silver, did not give any satisfactory results.

When we have to try for arsenic in the presence of phosphorus we can effect a sublimation by heating a mixture of the substance with soda and potassic cyanide. We can give a much greater sensitiveness to this operation by following the instructions which will be given later on (in § 21) when we are treating of the test for water.

The reaction with ammonic molybdate and nitric acid has the great fault of applying equally to phosphoric and arsenic acids. It possesses no advantages above the reaction just described, and it is extremely slow; we are, in fact, obliged, in dilute solution, to wait until the edge of the drop is dry. For this reason I prefer using chloride of ammonium and sulphate of magnesium. In conclusion, all that has been said about potassic phospho-molybdate applies also to ammonic phospho-molybdate.

18. Test for Chlorine.

The test for chlorine under the microscope cannot be made with nitrate of silver, as chloride of silver forms opaque clots and tufts, which have no particular characteristics, and might easily pass unobserved in cloudy solutions.

Mercuric nitrate under the same conditions gives rise to the formation of a crystalline precipitate composed of fine characteristic needles, which can be readily distinguished from the needles formed by gypsum; unfortunately these crystals change spontaneously after two or three minutes, and break up completely, forming particles of such minuteness that a magnifying power of 600 times is barely sufficient to enable one to distinguish that their transverse section is quadratic.

The salts of lead give crystalline needles distinctly formed and strongly refracting, with hydrochloric acid and soluble chlorides; but we cannot make use of this reaction when the chlorides are accompanied by sulphates. When we have effected the decomposition of the mineral by fusion with soda we can, in the majority of cases, advantageously use plumbic nitrate dissolved in dilute nitric acid as a reagent to indicate the presence of chlorine. The crystals of plumbic chloride separate from a cold solution in the manner which is familiar to everybody. The rhombs of plumbic chloride are about 10 to 15 microns in length; the dimensions of the dendrites vary considerably. The best plan of testing to be followed is that already described in § 16.

In the presence of sulphuric acid or of sulphates plumbic nitrate should be replaced by sulphate of thallium, a re-

agent which I much prefer to the salts of lead on account of the greater sensitiveness of its behaviour towards chlorides, and because of the immutability of the crystals of chloride of thallium.

In cases where we have attacked the mineral by fusing it with soda, we use sulphate of thallium dissolved in dilute sulphuric acid, following the plan just described (§ 16). In the majority of cases, however, it is preferable to use concentrated sulphuric acid, and to follow one of the two methods I am now about to describe. According to the first we decompose the mineral by heating it to a moderate temperature with as small as possible a quantity of concentrated acid, then add an equal volume of water, and then place a grain of sulphate of thallium in a small drop of water placed in contact with the liquid to be tested. The crystals of chloride of thallium then form in the immediate neighbourhood of the sulphate of thallium.*

All these operations are conducted on a glass plate. According to the second method we heat the mineral with a little rather stronger sulphuric acid in a platinum crucible and dissolve the hydrochloric acid, which is given off, in water. To effect this we must place a cover on the crucible with a small drop of water on its underneath side. This is cooled by putting a large drop of water on the top. After this micro-chemical distillation has been effected, the upper drop of water is removed by means of a capillary tube; we then turn over the cover and place it on the glass plate; we then place a small grain of sulphate of thallium in the drop. The crystals of chloride of thallium are not long in making their appearance; they consist of octahedra, and of combinations of octahedra with dodecahedra, having a diameter of 10 to 15 microns. Under a low power microscope, and by transmitted light, these crystals, on account of their high refrangibility, appear almost black, while they are white in direct light. This property, and still more the tendency to form triplets, or double twins like a cross, gives them a special character, and enables us to find very small and thinly distributed crystals.

The average length of the cruciform crystals is about 50 microns, but some are as much as 100 microns; they are very regular in formation, and closely resemble the cruciform crystals of magnesite which are found in scoria. The sensitiveness of the reaction depends on the quantity of acid contained in the liquid. It is for this reason that the crystals form much more quickly and in larger quantity when we use the second method than when we use the first. If the acid is in too great excess we can neutralise its baneful influence by adding an acetate, as has been already shown (§ 13).

Notwithstanding the loss, which is inevitable in attacking the mineral, and during the distillation of the hydrochloric acid, I have obtained a distinct reaction with a quantity of the acid corresponding to 0.004 m.grm. of chloride of sodium.

Bromide of thallium is hardly distinguished under the microscope from the chloride; the crystals have exactly the same formation in each case, and the colour is also the same; the dendrites of the bromide, however, are not so pronounced, and are only about 15 to 25 microns in length.

The iodide and fluoride of thallium are, on the contrary, quite distinct from the previous named salts. The crystals and the rosettes of the iodide, although of the same form as the chloride, are much smaller, the largest being only 20 microns in length, and they are of so strong a yellow colour that the tint can be distinguished in crystals of only 3 microns in length. By transmitted light these crystalline grains appear nearly black. The fluoride is more soluble than the other haloid salts of thallium;

it crystallises in very flat octahedra, and often forms combinations of the octahedron with the cube and the dodecahedron, when they even have the appearance of tablets of a very pale tint, and are very transparent compared with the chloride of thallium.

(To be continued).

INFLUENCE OF COPPER ON THE ESTIMATION OF SULPHUR.

By WM. F. BRUGMAN,
Chemist, Scranton Steel Company.

WHEN steel, pig-iron, or iron, is dissolved in HCl the sulphur present is given off as H_2S , a trace at most escaping the action of the solvent. Several devices are employed for absorbing and estimating the liberated H_2S , but all presuppose not only the completeness of the above reaction, but the assumption that all the H_2S is eliminated from the decomposing liquid. This might indeed be questioned when metals precipitable by H_2S are present in the material under examination, and reasoning from analogy one might expect that some of the sulphur would become inert through combination in the decomposing flask with such elements if present. Copper, on account of the comparative frequency with which it is encountered, merits our consideration in this respect more than the other members of this group, and some diversity of opinion seems to exist as to the accuracy of the " H_2S method" when this element is present.

G. Craig* shows that in the presence of copper no loss of sulphur is incurred. H. Rocholt† reaches the opposite conclusion, and after a series of experiments states that the loss is proportional to the amount of copper present. M. Troilus,‡ in a paper on the determination of sulphur in steel, says—"As for sulphur being retained in the residue as CuS , when the amount of copper is considerable, this is a matter of rare occurrence, and the presence of 1 per cent of copper or so would certainly be reason enough for a special searching investigation, not necessary during running work. A steel containing 0.30 per cent Cu gave 0.160 per cent S, both by the aqua regia and bromine (' H_2S method'), and a spiegel with 9 per cent Mn and $\frac{1}{2}$ per cent Cu gave traces of S by both methods." Again, he says§ "If the steel or iron contain much copper,—say more than 0.250 per cent, or other elements that are precipitated by H_2S in acid solution,—the bromine method is apt to give too low results."

A large proportion of the steels and pig-irons analysed at this laboratory contain high copper, and in view of the opinions expressed above I have deemed it imperative to institute a few experiments to satisfy myself as to the accuracy of the method|| used under these conditions.

	Per cent S.
A sample of pig-iron, containing 0.835 per cent Cu, gave by the "aqua regia method" ..	0.228
Fused with Na_2CO_3 and seppt., gave	0.226
Sulphur in same iron by " H_2S method" ..	0.228
A pig-iron, free from Cu, gave " H_2S method"¶	0.025
Determination repeated, after adding 0.035 Cu in the form of chloride, found	0.023
Sample of steel, containing 0.70 per cent Cu, gave (" H_2S method")	0.086
Repeated, adding to drillings 0.054 CuO , gave ..	0.087
Sample of steel, free from Cu, gave, same method	0.046
Same, after adding 0.054 CuO , gave, same method	0.048

* CHEMICAL NEWS, xlvii., 199 and 272.

† Ibid., xlvii., 236.

‡ Inst. Mining Eng., xii., 507.

§ "Notes on the Chemistry of Iron."

|| S. of M. Quarterly, v., No. 1.

¶ Five grms. used.

* We also obtain very good results by inverting the reaction for potassium. A mixture of platonic sulphate and sulphate of potassium renders very good service, but it is preferable to use a mixture of the acetates. This reaction is not more sensitive than that which is based on the use of sulphate of thallium, but it is much easier to observe.

In addition to the above I have repeatedly examined the solution remaining in the flask, and have never been able to detect a weighable amount of sulphur. These results show that copper exercises no deleterious influence, and can safely be disregarded when present to the amount of 1 per cent.—*School of Mines Quarterly*.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 282.)

Mr. EDGAR RICHARDS then presented a paper entitled—

Notes on a Comparison of the Official and Nitric Acid Methods for Phosphoric Acid Determination.

A discussion having arisen in the laboratory of this department in regard to the use of nitric acid as a solvent

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

in the determination of total phosphoric acid in fertilisers, I undertook some comparative experiments to determine the following points:—

Whether there was any difference in the results obtained between the two methods; and

Whether previous ignition with or without the addition of magnesium nitrate was necessary.

Nine samples of fertilisers were taken, eight of which were received from the committees of this Association. viz., Nos. 1—5, the samples sent out in 1885 by the Potash Committee, and Nos. 7—9, those received this year from the Phosphoric Acid Committee. No. 6, the remaining sample, was the one that occasioned the discussion.

The Tables below give the method of analysis followed and the results obtained.

The analyses show that the treatment of magnesium nitrate may be omitted, as it does not affect the results one way or the other; and the danger of losing an analysis by its spattering on ignition is avoided and time saved in

TABLE I.

Official Method.		Nitric Acid Method.	
1.	2.	3.	4.
Take 2 grms.	Take 2 grms.	Take 2 grms.	Take 2 grms.
Add 5 cubic centimetres Mg (NO ₃) ₂ and dry.			
Ignite.	Ignite.	Ignite.	
Heat with 15 c.c. HCl.		Boil with 10 cubic centimetres HNO ₃ .	
Filter and dilute to 200 c.c.		Filter and dilute to 200 c.c.	
Take 25 to 50 c.c. in duplicate.		Take 25 to 50 c.c. in duplicate.	
Neutralise with NH ₄ OH.		Neutralise with NH ₄ OH.	
Add 15 grms. Am. nitrate.		Add 50 to 100 c.c. Am. molyb. sol.*	
+ 50 to 100 c.c. Am. molyb. sol.*		+ 10 c.c. acid Am. nitrate sol.†	
Heat for 1 hour at 60° C. with occasional stirring.		Heat for 1 hour at 80° C. with frequent stirring.	
Filter and wash with dilute Am. nitrate sol.		Filter and wash with dilute acid Am. nitrate sol. (1 to 1).	
Dissolve with NH ₄ OH.		Dissolve NH ₄ OH dilute.	
Neutralise with HCl. Cool.		Neutralise with HCl. Cool.	
Add 5 to 10 c.c. Mg mixture, and 30 c.c. dilute NH ₄ OH.		Add 5 to 10 c.c. Mg mixture,* and 5 c.c. NH ₄ OH.	
Let stand 1 hour.		Let stand 1 hour.	
Filter, wash, ignite, and weigh Mg ₂ P ₂ O ₇ .		Filter, wash, ignite, and weigh Mg ₂ P ₂ O ₇ .	
* Fresenius's formula.		† { 650 c.c. HNO ₃ , sp. gr. 1·2. 70 c.c. NH ₄ OH, strong. 330 c.c. Water.	

TABLE II.—Comparison of Official and Nitric Acid Methods for P₂O₅.

	(1) Low-grade superphos- phate.	(2) High-grade phosphate.	(3) Tankage.	(4) Tobacco stems and ground bone.	(5) Ground bone.
(1) Official method	{ 9·776 9·750	11·324 11·337	12·079 12·027	11·567 11·464	20·319 20·268
(2) Official method, except treat- ment with Mg(NO ₃) ₂	{ 9·724 9·801	11·413 11·490	12·232 12·283	11·388 11·362	20·216 20·216
(3) HNO ₃ method	{ 9·801 9·776	11·439 11·490	12·233 12·207	11·618 11·567	20·396 20·421
(4) HNO ₃ method, except ignition	{ 9·827 9·852	11·464 11·516	12·156 12·104	11·362 11·336	20·268 20·268
Highest	9·852	11·516	12·283	11·618	20·421
Lowest	9·724	11·324	12·027	11·336	20·216
Difference	0·128	0·192	0·256	0·282	0·205

	(6) Tankage.	(7) South Carolina rock.	(8) Navassa.	(9) South Carolina and Navassa mixed.			
(1) Official method	{ 9·007 8·982	19·103 19·026	19·039 19·026	18·489 18·451	18·361 18·399	17·875 17·875	17·785 17·530
(2) Official method, except treat- with Mg(NO ₃) ₂	{ 8·879 8·879	18·758 18·860		18·604 18·553		17·734 17·713	
(3) HNO ₃ method	{ 8·995 8·095	17·313* 17·350*	17·043 17·018	18·374* 18·220*	17·657 18·092	16·897 16·813	16·828* 16·851*
(4) HNO ₃ method, except ignition	{ 8·956 8·892	19·090 19·244		18·886 18·962		18·349 18·297	
Highest	9·007	19·244	19·244	18·962	18·962	18·349	18·349
Lowest	8·879	17·018	18·758	17·657	18·361	16·813	17·530
Difference	0·128	2·226	0·486	1·305	0·601	1·536	0·819

getting a solution. Mere ignition at a low heat is enough to destroy all organic matter.

The nitric acid method without previous ignition of the fertiliser gives results that agree very closely with the official method, and though the solution may be highly coloured yet the organic matter is sufficiently oxidised to be harmless in the analysis. The solution is obtained in a very short time, and this method is much preferable for quick and accurate work.

When the fertiliser contains compounds of iron ignition renders these insoluble in nitric acid, and in such cases the destruction of the organic matter may be omitted, or the ignited substance may first be moistened with 2 c.c. hydrochloric acid before the addition of the nitric acid. In the results of Nos. 7 to 9, marked with an asterisk, hydrochloric acid was used, but in no other cases. In the case of South Carolina rock, however, this method of procedure did not give satisfactory results, as the table of analyses shows, but where the previous ignition was omitted the results were very good.

Instead of taking the trouble in the official method to weigh out 15 grms. of ammoniac nitrate each time, I make a concentrated solution of the salt, so that 10 c.c. of it are equivalent to the 15 grms.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 2nd, 1886.

W. H. PERKIN, Esq., Ph.D., F.R.S., Vice-President, in the Chair.

MR. Forbes Rickard was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Henry Downes, M.D., Chelmsford, Essex; George Arthur Goyder, Hawkers Road, Adelaide, Australia; E. Hori, 88, King Henry's Road, Chalk Farm, N.W.; Thomas Burdon Keay, 85, Herrington Street, Sunderland; Charles E. Sohn, jun., 25, Beverley Road, Anerley; James Pim Strangman, Sarno, Province of Salerno, Italy; Jokichi Takamine, Department of Agriculture and Commerce, Tokio.

The following were elected Fellows of the Society:— Messrs. James A. Audley; Chichester A. Bell, B.A., M.B.; John Williams Bevan; Cuthbert Robert Blackett; William B. Bottomley; Ebenezer John Cox; John Fuller; Alexander Galt; Thomas Forest Garwin; Sydney Joseph Harris; George Crompton Holt; H. E. Kirby; Henry A. B. Leissner; James B. L. Mackay; Hugh O'Donoghue Macan, B.A.; James B. Mackintosh; Edward Lloyd Marks; N. A. F. Moos; Herbert Pickington; L. S. M. Pyke; Edwin Quayle; James Schleselman; Harry Silvester; Arthur Turner; Alfred Hughes Twining; William Walker, Jun.; Reginald Williams.

The following papers were read:—

107. "Bismuthates." By M. M. PATTISON MUIR and DOUGLAS J. CARNEGIE,

The authors have attempted to isolate definite compounds of Bi_2O_5 , or Bi_2O_4 , with K_2O , but without success. They find that very long-continued washing with hot water is required to remove all the potash from the solid products of the reaction between BiO_3H_3 or BiOCl , very concentrated potash solution and chlorine. They show that $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ dissolves in about 100 times its weight of a boiling solution of KOH in a little water, and that yellowish white solids are obtained by nearly neutralising this solution; that these solids may be washed free from potash by boiling water, and that the residual

bodies then contain more oxygen than Bi_2O_3 , and nearly approach the composition Bi_2O_4 . They conclude that $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ exhibits feebly acidic functions in its reaction with a large mass of very concentrated potash solution; that under these conditions compounds of the form $x\text{Bi}_2\text{O}_5 \cdot y\text{K}_2\text{O}$ (or perhaps $x\text{Bi}_2\text{O}_4 \cdot y\text{K}_2\text{O}$) are probably formed, but that such compounds can only exist, if at all, in presence of large quantities of potash. The authors give reasons for regarding the formulæ given by C. Hoffmann (*Annalen*, ccxxiii., 110) to so-called potassium bismuthates as of little if any value.

108. "The Action of Inorganic Compounds on Living Matter." By JAMES BLAKE, M.D.

The reactions taking place between living matter and inorganic compounds have been investigated by introducing solutions of the substances directly into the veins and arteries of living animals. The action of compounds of more than forty of the elements have been investigated, and the following conclusions have been arrived at:— 1st. That the action of these substances on living matter is determined by the electropositive element. 2nd. That their general biological action is connected with their isomorphous relations, substances in the same isomorphous group causing the same biological reactions. 3rd. That in the same isomorphous group the intensity of biological action is determined by the atomic weight; the greater the atomic weight the smaller the quantity required to cause the same amount of biological action. The nature of these reactions is at present undetermined. They most probably are due to contact reactions.

DISCUSSION.

Mr. LLOYD asked whether Dr. Blake had experimented on vegetable matter, and if so, had he obtained similar results? Potash salts appeared to have an action altogether different from that of other members of the group; and it was known also that they affected plants in a special manner.

Dr. STEVENSON said that the subject of the communication was one of great interest, but beset with difficulties. Isomorphous substances often acted very differently upon the animal body, as for instance in the cases of sodium chloride and potassium iodide. Nor would the differences in the atomic weights of potassium and sodium account for the numerous differences in the toxic properties of their salts. Zinc sulphate and ferrous sulphate are isomorphous, but their physiological actions differ greatly. The magnesium group of metals were asserted by the author to act upon the vomiting nervous centre; but whilst this might be conceded as true of zinc and cadmium salts, magnesium salts were not usually regarded as emetics. We know so little of the molecular constitution of bodies in solution, that it was hazardous to reason from the isomorphism of solids to their analogies when in solution.

Dr. LAUDER BRUNTON regarded Dr. Blake as a pioneer in the field of pharmacology, and thought his paper interesting and instructive. The conclusions were, however, rather too general, and the exceptions deserving of more attention than Dr. Blake had given them. Thus the action of the chloride, bromide, and iodide of sodium is determined rather by the electronegative than by the electropositive element; and this is still more the case with the nitrites, all of which, both organic and inorganic, cause dilatation of the blood-vessels. The first-named salts also differ in action, although isomorphous. Again, the toxic power of elements does not rise regularly with their atomic weight, for sodium is less toxic than lithium; but potassium, though more toxic than sodium, is less so than rubidium. The body as a whole is a too complicated reagent, and instead of trying to arrange substances according to their lethal action on the body, a better result would be obtained, he thought, by investigating the effect of different substances on the constituent parts of the body, such as muscle, nerve, and nerve-centre.

Dr. BLAKE, in reply to a question by Mr. Newlands,

stated that he had not experimented on the therapeutic action of boracic acid. He had never before heard of the fact mentioned by Mr. Lloyd, that potash salts exercised an abnormal action on living vegetable matter. The observation was interesting, as of all the substances experimented with the potash salts were the only ones whose biological action was not in agreement with their isomorphous relations. This fact, however, cannot be regarded as an argument against his deduction that analogous actions were produced by isomorphous compounds, which was based upon the results of the examination of the biological action of forty-two other elements, potash salts forming in fact the only exception. The statement made by Dr. Stevenson, that the bromides, iodides, and chlorides of the same base differed in their physiological action, was a mistake, founded on imperfect methods of experimenting. His own experiments, as well as those of other observers, had shown that such was not the case. The remark by Dr. Brunton as to nitrous acid modifying the biological action of the base was undoubtedly true; pyrophosphoric and pyrovanadic acids also exerted a modifying influence, but he had shown that the sulphates, nitrates, phosphates, arseniates, carbonates, acetates, chlorides, iodides, and bromides of the same base caused the same biological reactions when introduced directly into the blood. To the remark of Dr. Stevenson that it was extremely improbable that compounds of such different elements as are contained in the same isomorphous group should cause the same reactions on the various organs, the speaker would only say that, however improbable such a fact might appear, yet experiment had clearly proved that such was the case. As an example that such was the case the action of the salts on the magnesium group was referred to, all of which act on the heart, on the vomiting centre, on the spinal cord, and on the blood, in exactly the same manner.

109. "Morindin and Morindon." By T. E. THORPE, F.R.S., and T. H. GREENALL.

Morindin was discovered by Anderson in the *Surangi*, the roots of *Morinda citrifolia*, which are extensively used in India as a dye-stuff, more especially for dyeing reds, purples, and chocolates. The substance occurs mainly in the root bark, and can be extracted by treatment with dilute alcohol, from which it crystallises in lustrous sulphur-yellow prisms. According to Anderson it has the formula $C_{28}H_{30}O_{15}$.

On heating in closed tubes it is decomposed, and yields a sublimate of *Morindon*, crystallising in long red needle-shaped crystals, to which Anderson assigned the formula $C_{28}H_{20}O_{10}$.

According to Rochleder and Stenhouse morindin is identical with ruberythric acid, $C_{26}H_{28}O_{14}$, and hence morindon is alizarin. Stein (*Fourn. Prakt. Chem.*, xcvi., 234) has, however, pointed out several facts which are inconsistent with this supposition. Morindin, like ruberythric acid, is a glucoside, but the product which it yields on hydrolysis, in addition to glucose, is not alizarin.

The authors have examined this question, and in the main their results agree with those of Stein. They extracted morindin from the roots of *Morinda citrifolia*, for a sample of which they are indebted to the Director of the Royal Gardens, Kew, and have compared its properties with those of ruberythric acid, obtained through the kindness of Dr. Schunck. The two substances are not identical, and they behave very differently on hydrolysis. Morindin gives, with sulphuric acid, ferric chloride, and on treatment with nitric acid perfectly different reactions from those afforded by alizarin. The analytical numbers obtained for morindin agree closely with those of Anderson; those obtained for morindon indicate that it is probably trihydroxymethylantraquinone. The quantity of the two products at the disposal of the authors was insufficient to definitely settle the constitution of the substances. Through the kindness of Mr. Wardle, of Leek, they have obtained a large supply of *M. citrifolia*,

and also of *M. tinctoria*, and a further communication on the subject is promised.

DISCUSSION.

Mr. GROVES said that he had assisted Dr. Stenhouse in the investigation referred to; it was not certain whether the species of *Morinda* examined was *citrifolia* or *tinctoria*. Also it was important to remember that a particular constituent might occur in a plant on one occasion and be absent in another sample, grown perhaps under somewhat different conditions. Thus Dr. Stenhouse had discovered *Munjistin* in the sample of munjeet he originally examined, but had altogether failed to find it subsequently in another sample, which, instead, contained another substance.

110. "The Hydration of Salts: Cadmium Chloride." By S. U. PICKERING.

Dr. Nicol has laid considerable weight (*CHEMICAL NEWS*, 54, 191) upon the fact that Thomsen (*Thermochem.*, 3, 201) has found the heat of hydration of cadmium chloride to be a negative quantity. This being the only inorganic salt which has a negative heat of hydration, the author has repeated Thomsen's work. Two samples were prepared of anhydrous salt, one at 200° C., and the other fused; they both gave numbers practically identical with that obtained by Thomsen, at 18°, -3011 cal. The hydrated salt also gave a number very nearly the same as Thomsen's, -760 cal., but was found to be a monohydrate instead of a dihydrate. Thomsen, therefore, in describing the salt used by him as containing $2H_2O$, has evidently made some error. The monohydrate is obtained upon evaporating a hot solution, and the dihydrate from a cold solution only. The dihydrate gives -2284 cal. on dissolution, and hence the heat of hydration of the salt is $CdCl_2 \cdot H_2O$ (solid) = 1092 cal., and $CdCl_2 \cdot 2H_2O$ (solid) = 2421 cal.

111. "The Decomposition of Sodium Carbonate on Fusion." By S. U. PICKERING.

The author has investigated sodium carbonate in the manner in which he investigated sodium sulphate (*Chem. Soc. Trans.*, 1884, 686), with a view to ascertain whether the discrepancies in the numbers given for its heat of dissolution could be accounted for by its existence in two modifications, as in the case of the sulphate. All specimens dehydrated at temperatures below the fusing point of the salt gave identical numbers, but the fused salt gave a result 200 cal. higher; this was traced to the decomposition of the carbonate: for on exposure to carbon dioxide that gas was absorbed, and the salt then gave a heat of dissolution 600 cal. less than the normal, owing to the formation of some of the acid carbonate, the necessary hydrogen having been derived from atmospheric moisture absorbed by the decomposed carbonate during its preparation. The amount of carbonate decomposed on simple fusion was about 3 per cent.

112. "Derivatives of Tolybenzene." By THOMAS CARNELLEY, D.Sc. (Lond.) and ANDREW THOMSON, D.Sc. (Edin.).

The preparation and properties of the following compounds are described:—

1. α -Monobromotolybenzene, $C_6H_5 \cdot C_6H_3Br \cdot CH = 1 : (2 \text{ or } 3) : 4$, m. p. 127—129°.

2. β -Monobromotolybenzene, $C_6H_4Br \cdot C_6H_4 \cdot CH_3 = 1 : 4 - 1 : 4$, m. p. 27—30°.

3. β -Monobromophenylbenzoic acid,—
 $C_6H_4Br \cdot C_6H_4 \cdot COOH = 1 : 4 - 1 : 4$, m. p. 193—194°.

4. α -Dibromotolybenzene, $C_6H_4Br \cdot C_6H_3Br \cdot CH_3 = 1 : 4 - 1 : (2 \text{ or } 3) : 4$, m. p. 113—115°.

5. α -Bromophenylbromobenzoic acid,—
 $C_6H_4Br \cdot C_6H_3Br \cdot COOH = 1 : 4 - 1 : (2 \text{ or } 3) : 4$, m. p. 202—204°.

6. β -Dibromotolybenzene, $C_6H_4Br \cdot C_6H_3Br \cdot CH_3 = 1 : 4 - 1 : (3 \text{ or } 2) : 4$, m. p. 148—150°.

7. β -Bromophenylbromobenzoic acid,—
 $C_6H_4Br \cdot C_6H_3Br \cdot COOH = 1 : 4 - 1 : (3 \text{ or } 2) : 4$, m. p. 231—232°.

Terephthalic acid was obtained as the final oxidation product of α -monobromoditolylbenzene, and parabromobenzoic acid as the final oxidation product of β -monobromoditolylbenzene, and of α - and β -dibromoditolylbenzene.

The two bromophenylbromobenzoic acids, melting respectively at $202-204^\circ$ and $231-232^\circ$, are isomeric and not identical with the dibromophenylbenzoic acid described by Hohn (*Ber.*, 16, 1082) since his acid was obtained from β -dibromofluorene ketone, and is therefore a derivative of 1:2 phenylbenzoic acid, whereas both our acids are derived from 1:4 phenylbenzoic acid.

113. "*The Amount of Chlorine in Rain-water collected at Cirencester*" By EDWARD KINCH, Royal Agricultural College, Cirencester.

Determinations of chlorine in the rain-water collected in a small 5 inch rain gauge, at the Royal Agricultural College, 443 feet above the mean sea-level, have been made continuously since 1870. The rain collected during the six months April to September is kept apart from that of the six winter months October to March; the chlorine is determined in the mixed waters of each six months.

The amount of chlorides in the rain is nearly always greater in the winter months than in the summer months. An abnormal amount of chlorides can generally be traced to storms from the south-west bringing salt spray from the Bristol Channel, about 35 miles distant. Crystals of common salt have been found after such storms on the windows of the College facing west. On one occasion, in September, 1869, Professor Church found chlorine equivalent to 6.71 grains of common salt per gallon in storm-water.

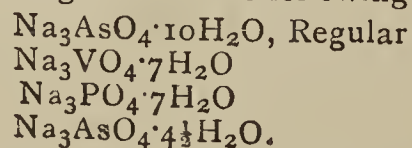
The rain collected during the winter six months, 1872-3, contained an abnormally large amount of chlorine; excluding this period the yearly averages for 16 years, 1870-1885, for the 12 years 1874-1885-86, also the means of the last 12 summer periods and 12 winter periods are—

	Rainfall in inches.	Chlorine per million.	Equivalent to NaCl per acre.
Mean of 12 summer periods to 1885	17.04	3.14	19.91
Mean of 12 winter periods to 1885-86	17.65	3.58	23.56
Average for 16 years (excluding winter 1872-73)	33.31	3.25	40.33
Average for 12 years to March, 1886	34.69	3.36	43.47

Lawes, Gilbert, and Warrington have found in the rain collected at Rothamsted, as a mean of six years' monthly determinations, 1.99 of chlorine per million, with a mean rainfall of 33.15 inches, equivalent to 24.59 lbs. of common salt per acre. They found the amount of chlorides in the summer months to be less than one-half that of the winter months.

116. "*Some Analogous Phosphates, Arsenates, and Vanadates*." By JOHN A. HALL, Student in the Laboratory of Owens College.

The author describes a number of phosphates and arsenates corresponding to the vanadates previously described by H. Baker (*Trans.*, 1885, 353); the salts of which an account is given are the following:—



114. "*Agricultural Experiments with Iron Sulphate as a Manure during 1886*." By A. B. GRIFFITHS, Ph.D.

The author and others have grown various crops with iron sulphate. Mr. Barlow (Oak Lane Farm, Whitefield, Manchester) after treating a plot of land of $\frac{1}{8}$ acre with 14 lbs. FeSO_4 , obtained 5287 lbs. of potatoes, while a similar plot without sulphate only yielded 4891 lbs.

Mr. J. J. Hunter (Newcastle-on-Tyne) states that he obtained a crop of turnips grown with FeSO_4 as good as a similar crop grown with guano and dissolved bones; he states "it will be far cheaper to use copperas." The author has tested the value of FeSO_4 as a manure for hay. Taking two plots of land of the same size, one manured with FeSO_4 gave 6962 lbs. of hay (dry), while the other not so manured gave only 3496 lbs. Mr. Barlow has found that iron sulphate is a good manure for onions. The author has grown mangel-wurzel crops with the ordinary artificial manures and top-dressing of nitrate of soda. Two plots were taken of the same size and treated alike as far as artificial manures, quantity of seed used, &c. One plot was dressed with $\frac{1}{2}$ cwt. FeSO_4 to the acre. This plot yielded 32 tons of roots; and the other plot (which was treated in precisely the same way, minus the FeSO_4) gave 26 tons of roots.

The author has grown for the third time bean crops. The land manured with FeSO_4 yielded 50 bushels of grain, while the other crop (not manured with FeSO_4) gave 30 bushels of grain. He also finds that iron sulphate is a good manure for palms and india-rubber trees. He recommends $\frac{1}{2}$ cwt. of FeSO_4 per acre as a top-dressing. The iron sulphate has proved to be an antiseptic agent of great value for parasitic micro-organisms. The paper shows that FeSO_4 is apparently a better manure (for certain crops at least) than kainite. With a top-dressing of $\frac{1}{2}$ cwt. of FeSO_4 the author obtained 9 tons potato tubers; and with 2 cwts. of kainite as a top-dressing only 6 tons of tubers. In all crops grown with the FeSO_4 , the albumenoids and soluble carbohydrates are increased. Concerning the ashes of the plants, it is found that when the iron manure has been used, the ferric and phosphoric oxides are increased, and the potash decreased, in the ashes of all crops.

Research Fund.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to make application before December 11th.

At the next meeting, on December 18th, the following Papers will be read:—

"Researches on the Constitution of 'Azo- and Diazo-derivatives.' I. Diazoamido-compounds." By R. Meldola, F.R.S., and F. W. Streatfield.

"The Influence of Silicon on the Properties of Iron and Steel." By Thomas Turner.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, December 6th, 1886.

HENRY POLLOCK, Esq.,

Treasurer and Vice-President, in the Chair.

THE following were elected Members:— Mrs. Lauder Brunton; Thomas Buzzard, M.D., F.R.C.P.; The Right Hon. Lord Thurlow, F.R.S.; Mrs. Annie S. Tweedie.

Seven Candidates for Membership were proposed for election.

The following Lecture arrangements were announced:—

Prof. Dewar, M.A., F.R.S.—Six Lectures (adapted to a juvenile auditory) on "The Chemistry of Light and Photography." On Dec. 28 (Tuesday), Dec. 30, 1886; Jan. 1, 4, 6, 8, 1887.

Prof. Arthur Gamgee, M.D., F.R.S.—Eleven Lectures on "The Function of Respiration." On Tuesdays, Jan. 18 to March 29.

Prof. A. W. Rücker, M.A., F.R.S.—Five Lectures on "Molecular Forces." On Thursdays, January 20, 27, February 3, 10, 17.

Three Lectures on Thursdays, Feb. 24, March 3, 10.

Prof. F. Max Müller, M.A., LL.D.—Three Lectures on "The Science of Thought." On Thursdays, March 17, 24, 31.

Carl Armbruster, Esq.—Five Lectures on “Modern Composers of Classical Song.” On Saturdays, Jan. 22, 29, Feb. 5, 12, 19.

The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.—Six Lectures on “Sound.” On Saturdays, Feb. 26, March 5, 12, 19. 26.

The presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

A Systematic Handbook of Volumetric Analysis; or the Quantitative Estimation of Chemical Substances by Measure, applied to Liquids, Solids, and Gases. Adapted to the Requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, &c., and for the Valuation of Substances used in Commerce, Agriculture, and the Arts. By FRANCIS SUTTON, F.C.S., F.I.C., &c. Fifth Edition. London: J. and A. Churchill.

THE fact that a new edition of this work—a fifth—has been called for only four years after the appearance of the former one proves that its utility and its merits meet with wide acknowledgment. The compass of the book has been somewhat extended, although certain matter which found place in the fourth edition has been eliminated. As such is mentioned the systematic volumetric process for the analysis of soils and manures, which is pronounced in the Preface to have been of little value, and the processes for determining the colouring-matter in indigo. These processes, as it was admitted in the last edition, whilst giving fairly accurate results with solutions of pure indigotine, are not trustworthy when applied where they are most wanted,—that is, to the indigos of commerce.

Among the principal additions figures the description of Kjeldahl's process for the determination of nitrogen, which has given “excellent results” in the author's laboratory.

The account of alkalimetric and acidimetric indicators has been enriched by an abstract of Mr. R. T. Thompson's researches (see CHEMICAL NEWS, xlvii.1, 23, 185, and xlix., 32, 119). Of the new indicators described in the former edition, several—*i.e.*, tropæolines OO and OOO, and eosine—have been omitted as not offering any distinct advantages, whilst lacmoid has been introduced into their room.

In the chapter on water-analysis the differences between the two editions are not very important. The determination of free oxygen in water, which many chemists class among the more important data for deciding the quality of a water-supply, which was not described in the former edition, is given on p. 230, quite separate from all the other instructions for the analysis of waters,—an arrangement of doubtful expediency.

The section on gas-analysis contains some very important improvements. Thus we may call attention to the description of Keiser's portable gas apparatus, Hempel's gas-burette, and Lunge's nitrometer, with their respective methods of use; and indeed all the paragraphs on simpler methods of gas-analysis, which are not to be found in the former edition.

Instructions for the volumetric analysis of glycerin, fats, and oils are also introduced for the first time. On the other hand, the process formerly given for the determination of guano has here been omitted.

As regards the determination of tannin the author has somewhat modified his opinion. In the former edition he writes (p. 276):—“Happily since that time Löwenthal has modified it [*i.e.*, his process], so that it may now be said to be worthy of trust, and much more satisfactory than any previous method.” In the present edition he

tells us—in our opinion with much greater correctness—that this method “is still deficient in accuracy or constancy of results, although much ingenuity and intelligence have been expended upon it.” A really trustworthy process for the determination of tannin would be indeed a boon. We doubt, however, whether any such process can be elaborated without a preliminary re-investigation of the tannins.

Two improvements in the getting up of the book deserve notice for their utility. The Index is much more elaborate and copious than heretofore, occupying sixteen columns as against eight in the former edition. In the previous edition the running heading at the top of the pages was simply “Handbook of Volumetric Analysis.” In the present we have “Volumetric Analysis” on the left-hand page, and on the right the chief subject dealt with on the page, which of course much facilitates the search for any particular subject.

As a whole this edition is a most decided improvement upon its predecessors.

Les Alcaloides d'Origine Animale (The Alkaloids of Animal Origin). By Dr. L. HUGOUNENG, Professor at the Medical Faculty of Lyon. Paris: Baillière et Fils.

THE author of this work remarks very justly that the discovery of the vegetable alkaloids presented at first considerable difficulties, and that the announcement of their existence and their properties was greeted with no little scepticism. Notwithstanding the wonderful advances of chemical science during the last half century, the recognition of the animal alkaloids encountered similar difficulties and similar doubts. And when the facts were admitted their import was still, and is still, misconceived. As the author remarks, very aptly, to make a discovery is sometimes easier than to understand its import. We shall err greatly if we suppose that the only result of the discovery of the animal bases is the introduction of a new difficulty, a new complication in chemico-legal investigations.

The researches of Selmi, Gautier, Etard, and Brieger and others have broken down an imaginary distinction between plants and animals. They have shown that the production of alkaloids is a general function common to all living cells, whether they be bacteria or the cells of living animals. They throw a new light upon the phenomena of life, of disease, and of death, as well as of putrefaction. Our healthy tissues live anærobically; a part, approximately one-fifth, of the decompositions of which they are the seat, is effected after the fashion of putrid fermentations. “During life, as well as during putrefaction, toxic alkaloids are produced; the kidneys, the bowels, all the natural emunctories have the task of their elimination, without which the organism is poisoned by its own products.” Hence, from one extremity of the chain of living beings to the other, biological chemistry henceforth assumes a striking character of unity; bacteria and the cellules of the highest organisms lead the same life, obeying the same laws, and leaving, as the residue of their activity, the same poisonous principles.

Dr. Hugouneng devotes the first portion of his treatise to the bacterian alkaloids and ptomaines. He explains their extraction by the methods of Stas-Otto, of Dragendorff, of Gautier, and Etard. These compounds he classifies as liquid and solid,—a distinction which we meet with in the vegetable bases,—and again as non-oxygenated and oxygenated. He points out the utter untrustworthiness of the reaction proposed by Brouardel and Boutmy for distinguishing the ptomaines as a class from the vegetable alkaloids,—*i.e.*, the reduction of potassium ferricyanide to the ferrocyanide. This reaction is not common to all the ptomaines, and it is observed with morphine, atropine, and certain artificial bases. Hence a general test, distinguishing all ptomaines from all plant-alkaloids and all artificial bases, is still to be sought for. The physiological action approximates closely to that of the pyridic

and hydropyridic bases. The following symptoms are given as resulting from the ingestion of these substances:—Rapid dilatation of the pupil, shortly followed by energetic contraction; reduction, and even abolition, of the excitability of the motor centres; loss of muscular contractility and of cutaneous sensibility, preceded by a brief period of tetanic convulsions; retardation of the movements of the heart, and drowsiness and torpor, frequently terminating in death.

Among the non-oxygenated ptomaines the author enumerates, as established, parvoline, hydro-collidine, two bases analysed though not named, collidine, neuridine, cadaverine, putrescine (which last three are not poisonous), and mydaleine.

The oxygenated alkaloids form a connecting-link between the ptomaines and the leucomaines, and all of them save gadinine are found in normal animal tissues, as well as in putrescent animal matter. Not a few of them, however, are violent poisons, such as neurine and muscarine.

Other alkaloids have been more or less distinctly observed, but they have not yet been isolated, and no account of their reactions, chemical or physiological, is therefore trustworthy.

The author then enters at some length into the toxicology of the ptomaines. He quotes the Commission appointed by the Italian Government to examine this question, who conclude that any given alkaloid may be distinguished from a ptomaine by a number of special characters which he enumerates. One point, however, appears not to have attracted attention. To name it might be indiscreet, as opening a new and unsuspected door for crime.

In the second part Dr. Hugouneng considers the physiological alkaloids, or the so-called leucomaines,—that is, those bases which are formed during life in the animal organism. These he divides into a uric and a creatinic group, besides a number whose composition and mutual relations are not thoroughly understood. Among the latter must rank the active principles of the poison of serpents. Here there is a necessity for much further research, which is impracticable in the United Kingdom on account of the "Vivisection Act."

As an Appendix we find a very complete bibliography of the subject, extending from 1849 down to the present year.

This work, as a fair and precise summary of the present knowledge on a most important subject, cannot be too highly commended.

Price List of Chemical Apparatus and Chemicals, &c.
Mawson and Swan, 11–15, Mosley Street, Newcastle-upon-Tyne.

WE have here a catalogue of laboratory appliances, which is, in some respects, well worthy of attention. It contains figures, descriptions, and prices of several pieces of apparatus not kept by all dealers, accompanied, in several instances, with instructions for their use. We notice here a set of apparatus for bacteriological researches, Stearn and Swan's patent compound Sprengel pump, a variety of aspirators, Swan's modification of Fletcher's anemometer for measuring air-currents in flues of chemical works, Schiebler's calcimeter, Stead's chromometer, Soxhlet's extraction-apparatus, Hogg's washing flask, Stead's apparatus for gas-analysis, gas-sampler, &c., the apparatus mentioned in Winkler's "Technical Gas Analysis," various nitrometers, Victor Meyer's vapour-density apparatus, and Von Schröder's apparatus, described in Proctor's work on tannin. There is also an extensive assortment of Fletcher's ingenious appliances for producing heat. On p. 13 in the description of balances a little confusion seems to have arisen from the insertion of decimal points where they are not wanted. Thus, we read of balances to carry 1'000, 1'500, &c., grains in each pan, the weights intended being obviously 1000, 1500, &c., grains respectively.

Among the list of chemicals and reagents figures magnesium sulphhydrate, which, on boiling, gives off 35 times its own volume of sulphuretted hydrogen, perfectly free from arsenic, from free hydrogen, and from acid fumes. Its advantages in analytical work, and especially in toxicological investigations, cannot, therefore, be questioned.

We perceive that Messrs. Mawson and Swan likewise issue catalogues of electrical and physical apparatus, of microscopes and other accessories, and of photographic apparatus and appliances.

CORRESPONDENCE.

THE TEACHING OF SCIENCE IN SCHOOLS.

To the Editor of the Chemical News.

SIR,—Sir James Paget at the University of London, in distributing the prizes and certificates to successful candidates at the London centre for the Oxford Local Examinations, on Wednesday, December 1st, took as the subject of his address the Teaching of Science in Schools. Those interested in the matter will find the report in the *Times* of December 2nd. Some quotations from it are given below for the convenience of readers who have not the report at hand.

"But as a man of science himself he was not prepared to admit that the study of classics or of literature was a more efficient instrument for the training of the mind's powers than the study of natural science. But he could not but observe and regret the exceedingly small number of candidates who submitted themselves for examination in science. He thought the schools were making a great mistake in not offering greater encouragement to scientific studies. . . . But the schools were far behind except in a few of the large manufacturing towns. . . . It was therefore of the first importance that science should obtain as full a recognition in schools as any other subject.

. . . In the sixth forms science was generally thought a hindrance. Let the schools take warning in time. Science must have its due position assigned to it in our schools, and masters must be appointed equal in power and position to any of the other masters."

"The number of persons of scientific attainments who were in request was constantly increasing. He was a member of the Council of the Health Exhibition, and he remarked on the large number of scientific persons employed. He asked, 'Where do you find them all?' The answer was 'Oh, they are all Germans.'"

With regard to the last statement it is hardly matter for wonder that—with an almost entire absence of technical education, and our public schools overstocking the market with oftentimes indifferent mathematical and classical students, forced into these two grooves by the boycotting of Science—foreign labour competes with a degree of success which proves inconvenient, if not disastrous, to the prospects of a tyro in Science.

Two causes are perhaps worthy of regard whilst considering the failure in School Science-teaching:—

1. That the appointment of the Science-master, and the portion of time allotted to him during the week, are under the control of Classical and Mathematical masters, who regard Science with disfavour, or at best with indifference.
2. That in many cases laymen are appointed as Science masters.

Even the ardour of a boy thirsting for knowledge may be damped by a series of unsuccessful experiments and recourse—*faute de mieux*—to prolonged black-board calculations.

With some notable exceptions, are the names of Science masters (having much leisure for research) found in our scientific journals as often as could be wished?—I am, &c.,

CHRONONHOTONTHOLOGOS.

MONSIEUR PASTEUR ON VIVISECTION.

To the Editor of the Chemical News.

SIR,—I enclose you a copy of a letter from M. Pasteur to a friend of mine, Mr. A. H. Bygott, of Lincoln. The letter may interest physiological chemists.—I am, &c.,

A. B. GRIFFITHS, Ph.D., F.R.S. (Ed.), &c.

Lincoln School of Science,
December 3, 1886.

“Paris, le 12 Nov., 1886.

“MONSIEUR,

“Vous trouverez les dernières statistiques publiées sur la rage dans la brochure que je mets à la poste en même temps que cette lettre.

“(Lecture faite le 2 Nov. aux Académies des Sciences et de Médecine à Paris.)

“Pour le charbon c'est environ cinq cent mille animaux, bœufs, vaches, moutons, qui sont vaccinés en France chaque années.

“Vous me demandez en outre mon opinion sur la vivisection :—

“Une pareille question ne devrait pas être discutée. Je condamnerais à l'égal de la femme la plus sensible la barbarie dans la vivisection, mais qui est donc le savant digne de ce nom à qui on pourrait reprocher cette barbarie? Quant à s'apitoyer sur la mort de quelques lapins lorsque le but est de sauver la vie d'un homme, quant à faire du sentiment devant le sacrifice de quelques moutons pour sauver des moutons et des bœufs par centaines de mille, il n'y a que des insensés qui puissent raisonner ainsi.

“Recevez l'assurance de ma considération très distinguée,

“L. PASTEUR.”

THE FADING OF WATER-COLOURS.

To the Editor of the Chemical News.

SIR,—In the course of some experiments on the action of sunlight on water-colour paints, I found that some mineral colours which did not contain “lead or mercury” were far from permanent when exposed to daylight in the presence of moisture.

The paints experimented on (Windsor and Newton's moist water-colours) were brushed thickly over Whatman's best drawing-paper, and exposed in an atmosphere of dry and of damp air to the action of daylight, one half of each strip being protected from the action of the light.

Cadmium yellow in damp air was entirely bleached on the parts exposed to light in two weeks, but remained absolutely unaltered in dry air.

Prussian blue in damp air was entirely bleached after four weeks' exposure, remaining permanent in dry air.

Yellow ochre faded slightly in the presence of moisture after four weeks' exposure, no change being observed in dry air.

In the case of the organic colours experimented on—viz., crimson-lake, rose-madder, gamboge, and indigo,—the colours were discharged as rapidly in dry as in damp air.

That the fading of cadmium yellow (cadmium sulphide) was caused by oxidation of the yellow sulphide to the white sulphate was shown by treating the bleached paper with water slightly acidified with hydrochloric acid; on adding sulphuretted hydrogen water to one portion of this solution the yellow sulphide of cadmium was precipitated, whilst the other portion gave a white precipitate of barium sulphate on addition of barium chloride.

These experiments have been carried on within the last two months, during which time the light has been very feeble.—I am, &c.,

ARTHUR RICHARDSON.

University College, Bristol,
December 1, 1886.

AN EXAMINATION PUZZLE.

To the Editor of the Chemical News.

SIR,—Permit me to ask A. X. if he has ever heard of such a substance as sodium silicate, or of sodium aluminate, and to inform him that the former of these, if in dilute solution, is not precipitated by hydrochloric acid; the latter, if exactly neutralised, yields a precipitate which is immediately dissolved by excess of acid.—I am, &c.,

A. P. S.

December 4, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 21, November 22, 1886.

On Ammonium-Magnesium Phosphate.—M. Berthelot.—It appears that ammonia, when acting upon tri-magnesium phosphate, must produce thermic effects which are very feeble, and precisely of the kind as those which it produces when acting upon the soluble magnesium salts. It is seen at the same time that ammonia, jointly with magnesia, forms, as regards phosphoric acid, a complex base comparable, in its energy, to potassa and soda. Tri-magnesium phosphate in the colloidal state may be rapidly changed into ammonium-magnesium phosphate by the action of ammonia, not because this latter phosphate in the colloidal state exceeds the former in the heat liberated, but because the double phosphate passes more rapidly than the simple phosphate into the crystalline state, with a further liberation of heat.

Actinometric Studies.—E. Duclaux.—Physicists have, for a long time, been seeking for a good process for measuring the chemical action of the sun's rays, which should not be liable to the influence of the thermic action which is generally superadded to the actinic effect. The author utilises, for this purpose, the solar combustion of dilute solutions of oxalic acid. With certain precautions, such as using flat vessels into which the same quantity of acid is always introduced, and taking a solution of 3 grms. per litre, the results are very constant.

New Process for the Volumetric Determination of Zinc-Powder.—F. Weil.—This paper will be inserted in full.

Action of the Alcohols upon Gold-Phosphorus Chloride.—L. Lindet.—The action of the alcohols upon the double chloride of gold and phosphorus gives rise to numerous organic compounds, always containing a molecule of aurous chloride. The author views these compounds as ethers derived from a “chlauroso-phosphorous” acid, $\text{Au}_2\text{ClPH}_3\text{O}_6$. In this paper M. Lindet describes the preparation and properties of the ethylic and methylic ethers of this acid.

On the Russian Petroleums.—J. A. LeBel.—The very volatile portions of the oil of Tschungnalek are absolutely similar to those of the oils of Bakou; the differences becoming accentuated only towards 150° . The fractions of Russian petroleum volatile below 60° do not contain any naphthenes, a fact which confirms the conclusions of Beilstein and Kurbatow relative to their identity with the benzene hydrides.

Neutralisation-Heats of Malic and Citric Acids and their Pyro-derivatives.—MM. Gal and Werner.—It results that the total neutralisation-heat of the pyro-acids, excepting the itaconic, is superior to that of the original acids by about two calories. We see here a

relation analogous to that observed between the mono-basic acids and the corresponding acid-alcohols. The pyro-acids derived from malic acid by the elimination of H_2O , and from citric acid by the elimination of $H_2O + CO_2$, no longer contain the group OH .

Journal für Praktische Chemie.

New Series, Vol. xxxiv., Parts 8 and 9.

Influence of certain Neutral Salts upon the Catalysis of Methyl-acetate of Hydrochloric and Sulphuric Acids.—H. Trey.—The rapidity of the reaction of hydrochloric acid is increased by the presence of its neutral salts; with sulphuric acid the reverse holds good. No numerical relations were manifested for the influence of different salts. If there appears a certain dependence on the atomic weight, no general conclusions could be drawn on account of the small number of the salts examined.

Studies on Diastase.—C. J. Lintner.—Although diastase differs in its composition from the albumenoids, a great similarity to the latter appears in its other properties. As diastase appears in greatest abundance in germination, and as the chemism of germination is, in a certain sense, to be interpreted as a process of oxidation, the conjecture lies near at hand that diastase is an oxidation product of certain protein compounds. That not all protein matters are equally disposed to yield diastase appears from the fact that the seeds of those cereals which are richest in protein do not yield most diastase on germination. The author uses the term "enzymo" as a convenient general name for chemical ferments in contradistinction to the figured or organised ferments.

Contributions to the Chemistry of the Rhodium-Ammonium Compounds.—S. M. Jørgensen.—This valuable paper contains a copious account of the roseo-rhodium, nitrate-purpureo-rhodium, and xantho-rhodium salts. In all these three groups there appears an evident analogy between the cobalt, chrome, and rhodium compounds. But the xantho rhodium salts are far more stable than the corresponding salts of cobalt and chrome. That the nitrous acid of the xantho-rhodium salts cannot be expelled in the cold, even by strong sulphuric acid, and cannot, indeed, be recognised as such, shows with certainty that the xanth-salts are nitrite-purpureo salts, which is confirmed by the very closely approximating crystalline forms of the xantho-fluosilicates and the haloid purpureo-fluosilicates, as well as by the analogous composition of the acid sulphates.

Apparatus for Chemical Laboratories.—Dr. Joh. Walter.—The descriptions of the apparatus cannot be made intelligible without the accompanying figures.

Bulletin de la Société d'Encouragement.

Series 4, Vol. i., No. 9, September, 1886.

Production of Aluminium and its Derivatives in the Electric Furnace.—E. Combes.—From the *Journal of the Franklin Institute*.

Preparation of Ortho-Phosphoric Acid, and Titration of Phosphoric and Arsenic Acid by means of Various Indicators.—A. Joly.—From the *Comptes Rendus*.

MISCELLANEOUS.

Owens College, Manchester.—Mr. Harold B. Dixon, M.A., F.R.S., Fellow of Balliol College, Oxford, has been appointed Professor of Chemistry and Director of the Chemical Laboratories in succession to Sir Henry E. Roscoe, M.P.

Royal Institution of Great Britain—The Christmas Lectures.—A course of six lectures (adapted to a juvenile auditory) on "The Chemistry of Light and Photography" (with experimental illustrations), will be delivered by Professor Dewar, M.A., F.R.S., Fullerian Professor of Chemistry, R.I., Jacksonian Professor of Natural Experimental Philosophy, Cambridge, on the following days, at three o'clock:—Lecture I., Tuesday, December 28th, 1886; Lecture II., Thursday, December 30th; Lecture III., Saturday, January 1st, 1887; Lecture IV., Tuesday January 4th; Lecture V., Thursday, January 6th; Lecture VI., Saturday, January 8th.

Guthrie Memorial Fund.—The following letter is being circulated amongst a large number of scientific men who knew the late Professor Guthrie. We gladly reprint it here, hoping that it may thus meet the eyes of others who will be willing to contribute towards a very deserving object:—"Many of those to whom this letter is sent will feel that by the death of the late Professor Guthrie, F.R.S., whose simple character and wide sympathies endeared him to a large circle of attached friends, they have sustained a personal loss. His time was exclusively devoted to teaching and to scientific research: unfortunately the provision for his family is far from adequate. His widow is anxious to provide for the education and maintenance of her step-children, but the slender income furnished by a policy of insurance settled on herself will not enable her to do this. The ages of the children dependent upon her are twelve, fourteen, and seventeen years, respectively, and their case is the more sad because, until a late period of his life, Dr. Guthrie had every reason to be satisfied that they were sufficiently provided for. Under these circumstances it will be felt by all who value his memory, as well as by those who only knew him through his scientific labours, that any sum which is gathered as a memorial of his life must necessarily be devoted to placing his children as nearly as may be possible in a position they would have occupied but for his untimely death, and to supplementing the provision for his widow. A committee has accordingly been formed, under the presidency of Professor Huxley, to raise a fund for the purposes here indicated. The committee trust that you will allow your name to be added to the list of subscribers, and that they may count upon your active support. Subscriptions may be sent to the Honorary Treasurer, Major C. A. Macgregor, R.E., Science Schools, South Kensington Museum, London, S.W.; or to the Honorary Secretary of the Fund, Mr. C. Vernon Boys, at the same address. Cheques to be crossed 'Messrs. Cox and Co.'"

MEETINGS FOR THE WEEK.

MONDAY, 13th.—London Institution, 5.

— Medical, 8.30.

— Society of Arts, 8. (Cantor Lectures). "The Principle and Practice of Ornamental Design," by Lewis Foreman Day.

TUESDAY, 14th.—Institution of Civil Engineers, 8.

— Photographic, 8.

WEDNESDAY, 15th.—Society of Arts, 8. Adjourned Discussion on Dr. C. Meymott Tidy's Paper on "Sewage Disposal."

— Meteorological, 7.

— Geological, 8.

THURSDAY, 16th.—Royal, 4.30.

— London Institution, 6.

— Chemical, 8. "Researches on the Constitution of 'Azo- and Diazo-Derivatives'—I. Diazo-amido Compounds," by R. Meldola, F.R.S., and F. W. Streatfeild. "The Influence of Silicon on the Properties of Iron and Steel," by Thomas Turner.

ERRATA.—In Report of Physical Society's meeting, p. 282, col. 2—At line 10 from top, for "y" read "γ." Line 23, for "y" read "q."

Line 24, for "q" read "y." Line 28, for $t \frac{dx}{dt}$ read $L \frac{dx}{dt}$.

THE CHEMICAL NEWS.

VOL. LIV. No. 1412.

ON THE VOLUMETRIC DETERMINATION OF CHROMIUM.

By W. J. SELL, M.A., F.I.C.,
Demonstrator of Chemistry in the University of Cambridge.

WHEN an aqueous solution of any chromic salt is mixed with excess of potash, to which a small quantity of hydrogen dioxide has been added, the mixture gradually changes in colour from green to yellow, the chromium sesquioxide being converted into chromate. This change is accelerated by heat, and is apparently complete on boiling for a minute or two. The following equation represents the reaction:—



The possibility of utilising this reaction as the basis of a rapid and convenient method for the quantitative estimation of chromium led to an examination being made in the first instance of its application as a volumetric process.

The following is a brief description of the method employed in the examination of this question, together with the results obtained by its application.

A solution containing a known weight of chrome-alum was mixed with sufficient potash to re-dissolve the precipitate first produced, a solution of hydrogen dioxide added, and the mixture boiled briskly for at least fifteen minutes. In the alkaline solution of chromate thus obtained the chromic acid was estimated by the iodometric method (Tulkowsky's modification), though it may be noted that any of the ordinary methods will do equally well.

(1) In presence of alumina. The chrome-alum employed was mixed with about an equal weight of aluminium sulphate.

0.75542 gm. required 51.5 c.c. thiosulphate (each c.c. = 0.00151 Cr) = 10.37 per cent Cr.

0.75542 gm. required 49 c.c. thiosulphate (each c.c. = 0.00163 Cr) = 10.46 per cent Cr.

(2) In presence of zinc. About 1 gm. of zinc sulphate was dissolved in the potassic dichromate used.

50 c.c. N/10 dichromate reduced by sulphurous acid, and, after boiling off excess of the latter, oxidised by method, required 68.6 c.c. thiosulphate, or practically the same volume as by direct titration.

(3) In presence of iron. As ferric salts liberate iodine from potassic iodide it was obvious that some modification of the process, as previously carried out, would be necessitated. The most obvious, perhaps, was to filter off the ferric hydrate after oxidation, and determine the chromic acid in the filtrate by the iodometric method, as before. This was tried with the following results:—

0.60579 gm. chrome-alum, mixed with ferric chloride, required 36.4 c.c. thiosulphate (1 c.c. = 0.001709 Cr) = 10.26 per cent Cr instead of 10.49.

50 c.c. N/10 dichromate, mixed with ferric chloride, reduced by sulphurous acid, and oxidised again by method, required 67 c.c. thiosulphate instead of 68.5 c.c.

50 c.c. N/10 dichromate, similarly treated, required 66.8 c.c. thiosulphate.

A glance at the results obtained so far will show that chromium sesquioxide is completely oxidised to chromate by the foregoing process, and that it may be successfully employed for the estimation of the substance either alone or in presence of salts of aluminium or zinc. In the case of iron the results are low, owing to traces of chromium hydroxide escaping oxidation. The question as to how this difficulty may be surmounted and the examination of the influence exerted by the presence of some other substances is at present engaging my attention.

As a solution of hydrogen dioxide has become a regular laboratory reagent, I may perhaps, in conclusion, point

Weight of Chrome-alum taken.	No. of c.c. Thiosulphate required.	Value of each c.c. Thiosulphate in Cr.	Cr indicated by method.	Percentage of Cr in Chrome-alum found.	Percentage of Cr in Chrome alum calc.
0.60579 gm.	37.2	0.001709	0.06357	10.49	10.49
0.60579 „	37.4	„	0.06391	10.56	10.49
0.60579 „	37.6	„	0.06425	10.60	10.49
0.5677 „	39.5	0.00151	0.05964	10.50	10.49
0.75542 „	53	„	0.08003	10.59	10.49
* 0.75542 „	53.1	„	0.08018	10.61	10.49
1.0159 „	66.6	0.001613	0.10742	10.57	10.49
† 0.7889 „	56.9	0.00151	0.0859	10.89	10.49

* To this lot, after addition of the oxidising mixture and boiling for ten minutes, a small quantity of platinum black was added and the boiling continued for a further period of ten minutes.

† This lot was only boiled ten minutes after addition of oxidation mixture.

Some additional experiments were made with N/10 potassium dichromate by determining iodometrically the number of c.c. of thiosulphate required for 50 c.c. dichromate, and comparing the result with that obtained from similar portions of the same dichromate solution after reduction with sulphurous acid and oxidation by method.

	Thiosulphate.
(1) 50 c.c. dichromate required	68.5 c.c.
(2) „ „ „ „	68.6 „
(3) Ditto, after reduction and oxidation..	68.6 „
(4) „ „ „ „	68.2 „

Two other experiments, in which potash was replaced by sodium carbonate, gave equally satisfactory results.

Attention was now directed to the question as to how far the accuracy of the process was influenced by the presence of other metals. I am unable at present to give a complete answer to this question. The following experiments were made:—

out how this reaction may be utilised in qualitative analysis for the separation of the metals of Group III., viz., those precipitated by ammonia.

The precipitate after washing is dissolved in the least possible quantity of dilute nitric acid and poured into an excess of potash, to which a few cubic centimetres of hydrogen dioxide have been added. The mixture is then boiled for three or four minutes and filtered. The precipitate contains the iron, phosphates, traces of manganese, &c., which is detected as usual. The filtrate, containing all but the least trace of chromium as chromate and the whole of the alumina, is divided into two parts. Part I. is acidified with acetic acid and tested with lead acetate; II. is tested for alumina by NH_4Cl as usual. I may add that test experiments have given the most satisfactory results.

PS. Since the above was sent for publication my attention has been drawn to a paper in the June number of the

Bull. Soc. Chem., by M. Martinon (an abstract of which appears in the last number of the *Journ. Chem. Soc.*), in which the author announces the discovery of the reaction here used, but makes no attempt to utilise it analytically. The bulk of my work was done before the appearance of M. Martinon's paper, but its publication was deferred from time to time in the hope of finding leisure for its completion.—W.J.S.

NOTE ON THE EXISTENCE OF IODINE IN THE FREE STATE IN A MINERAL WATER.

By J. ALFRED WANKLYN.

It has been known for many years that the water of the Woodhall Spa, near Lincoln, is exceptionally rich in bromides and iodides. In the course of an investigation I have made the observation that there is free iodine in this water, and not a mere trace of free iodine, but sufficient to impart to the water a brown colour of considerable depth of tint.

A very instructive experiment is to shake up the water with about one-twentieth of its volume of bisulphuret of carbon, whereupon the brown colour will leave the water and the bisulphuret of carbon will assume a rich violet colour.

The Woodhall Spa is known as a remedy in skin diseases; and no wonder that it should be, since it is a solution of free iodine.

ON THE ESTIMATION OF NICKEL IN MATTES, ORES, SLAGS, &c.

By THOMAS MOORE.

In the following remarks I shall deal only with the separation of nickel from iron, aluminium, chromium, and manganese, the other metals generally accompanying it being those precipitable by H_2S , such as copper, arsenic, antimony, &c., and inasmuch as they may be all got rid of at once by the application of that gas their further consideration is unnecessary.

The main difficulty now remaining is the separation of the nickel from the iron when the latter metal is present in considerable quantities. The most simple process is that recommended by Wöhler, precipitating the solution containing ammoniac chloride by excess of ammonia, dissolving the precipitated ferric hydroxide and repeating the precipitation and solution so long as the filtrate contains nickel. By this process all the nickel is, without doubt, obtained, but the repetition of the process requires a considerable time, and the solution is loaded with ammoniacal salts, so that it is necessary to precipitate the nickel as sulphide; a tedious and somewhat uncertain operation. Field's process by boiling the solution of the nitrates with oxide of lead cannot be recommended, as the ferric oxide invariably contains nickel. When the iron is thrown out as a basic salt it is equally necessary to repeat the precipitation, and this gives a very large filtrate to deal with, especially when the basic acetate method is employed, and, moreover, if the solutions are not neutralised to the correct degree the separation may prove a failure.

Now by employing the electrolytic method for the precipitation of nickel, it is not necessary that the iron be completely eliminated, a small quantity having no appreciable influence on the results, as it simply floats as the insoluble oxide in the ammoniacal solution. In those cases, therefore, when only the nickel is to be estimated, I have found it best to precipitate the iron as phosphate from an acetic acid solution, in which it is but very slightly

soluble, whilst the corresponding nickel compound dissolves with the greatest of ease. For ordinary technical purposes only one precipitation is necessary, but when greater accuracy is required it is best to repeat the precipitation. The advantages to be obtained by using this method in place of those already mentioned are: no neutralisation necessary, comparatively small filtrate from which the nickel is readily precipitated, and, as a consequence, more rapidly obtained results. The following are the working details of the process which I have employed successfully for a considerable period. Dilute the strongly acid solution (it is immaterial whether sulphuric, hydrochloric, or nitric acid) with water to about 250 c.c., then add an excess of sodic phosphate; if a precipitate forms add acid till it dissolves, raise to the boiling-point, and whilst boiling add sodic acetate solution until the iron is all precipitated as a very pale yellow phosphate; then boil for a minute and filter, wash well with hot water containing a little sodic acetate and acetic acid. The filtrate is now warmed and treated with potassic hydrate and bromine; this throws down the nickel as peroxide, which may be readily filtered off and well washed with hot water. The peroxide is then dissolved off the filter in dilute warm sulphuric acid, from which solution the nickel is electrolytically deposited, first rendering it strongly alkaline with ammonia. A small quantity of ferric hydroxide will probably be found floating in the electrolyte; but this, as already mentioned, does not influence the results. Aluminium remains with the iron, whilst chromium and manganese are to be found in the solution after the deposition of the nickel is completed; the manganese being partially thrown down as peroxide on the anode, whilst the chromium is simply converted into a chromic salt.

Erdington, Birmingham,
Dec. 7, 1886.

ON CERTAIN COLOURED REACTIONS OF TITANIC, NIOBIC, TANTALIC, AND STANNIC ACIDS.

By M. LUCIEN LEVY.

THE recognition of the titanic, niobic, and tantalic acids, especially in presence of each other or of stannic acid, is a difficult problem, offering a very limited number of solutions. Every novel specific character of these acids seems, therefore, of importance.

The reagents employed by the author present, for the most part, a phenolic function, and, reciprocally, these latter bodies may, in their turn, be recognised by means of these same mineral acids.

The method of procedure is as follows:—A trace of the reagent (more than $\frac{1}{4}$ m.g.), is placed in a watch-glass, moistened with 8 drops of sulphuric acid, and some granules of the dust of the acid under examination, or of one of its salts are added. In case of stannic acid it is necessary to take a rather large quantity and to add a little water to the mixture. The results obtained are laid down in the accompanying tables. (See next page).

With the exception of those produced by stannic acid all these colours disappear on adding a few drops of water; only the colourations derived from brucine do not yield a colourless solution, the fiery red of the sulphuric solution of brucine remaining after dilution. It is necessary to operate with substances quite free from nitrous or nitric acid; the nitrous vapour liberated by sulphuric acid yields, under the conditions of the experiment, derivatives of a very intense colouration. The table shows that the reagents employed possess one or more phenolic functions, although brucine has not hitherto been regarded as a phenol. Acids, alcohols, aldehyds, acetones, quinones, and alkaloids devoid of phenolic functions do not produce a colouration. This at least,

Reagent.	Titanic Acid.	Niobic Acid.	Tantallic Acid.	Stannic Acid.
Morphine	Crimson	—	Yellow, then brown	—
Codeine	—	Mauve after some time	Watery green	—
Brucine	Slight crimson	Café au lait	Tea-rose	—
Phenol	Brick red	Yellow	Rose, then green, turned to rose by H ₂ O	—
Naphthol α	Greenish, then violet	Green, then slate-grey	Scheele's green	Amethyst
Naphthol β	Burnt coffee	Gamboge	Greenish	Apple green
Thymol	Garnet	Flesh, then brown	Yellow, green, then olive	Light rose
Resorcine	Flesh, then chocolate	Yellowish	Dirty grey, amethyst, then rose	Orange
Hydroquinone	Crimson	Dirty grey, then violet mauve	Greenish, then yellow	Light yellow
Pyrocatechine	Chocolate	Pearl grey	Greenish	—
Pyrogallol	Crimson, then brown	Greenish grey	Ditto	Tea rose
Salicylic acid	Flesh, then brick red	Rose, then flesh	Ditto, black the next morning	—
Oxybenzoic acid } (meta)	Chrome yellow	Light yellow	Very pale yellow	—
Oxybenzoic acid } (para)	—	—	Ditto, gooseberry the next day	—
Gallic acid	Brick red	—	—	—

is the result of experiments made with a great number of very various substances.

Certain derivatives of the phenols likewise act upon titanlic acid. Thus, phenylsulphuric acid gives an orange and triphenyl a tea-rose colour. Here must also be referred the colours yielded by various carbides. There are formed first sulpho-conjugated compounds; thus, benzene added little by little, gives a reddish-yellow colouration, toluene, a colour of café au lait; and naphthalene a pale violet colour, turning grey.

Silica, alumina, zirconia, and uranium oxide (yellow) under the same conditions, do not give rise to any visible phenomenon.

The coloured reactions above described render it possible to detect titanlic, niobic, tantallic, and stannic acids, even if mixed together. The following seems the best procedure:—Ignite the mixed salts in question with ammonium carbonate to destroy every trace of nitric acid; treat a portion of the mixture, as indicated above, with morphine; a crimson colour indicates titanlic acid; try the codeine reaction on another part of the mixture; a mauve colour betrays niobic acid: try a third portion with resorcine; an amethyst violet (or green, if there is much of the two acids present) shows tantallic acid; a last part of the mixture, if it gives an amethyst violet with α -naphthol and water, reveals stannic acid.

These same reactions furnish, likewise, several methods for the detection of certain phenols. For instance, in a mixture of morphine and codeine, titanlic acid shows even a trace of morphine and niobic acid indicates codeine.—*Comptes Rendus*, ciii., p. 1074.

MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Continued from page 290.)

19. Test for Fluorine.

IN testing for fluorine it is first necessary to transform it into hydrofluosilicic acid: in order to effect this we first separate it in the form of silicic fluoride by distilling with concentrated sulphuric acid; in some cases it is necessary to add a little silicic acid or powdered glass.

Certain fluoric silicates, such as the topaz (tourmaline) and pyknite, ought to be first of all attacked by fusion with carbonate of soda (two parts of the latter to one part of the mineral). Fusion with hydrosulphate of potash, or with the salt of phosphorus, might serve equally well to separate the fluorine from the mineral, but the

temperature necessary to effect this decomposition is too high.

The silicic fluoride which is formed is absorbed by dilute sulphuric acid, which does not evaporate so quickly as pure water; instead of the cover which was used in the distillation of hydrochloric acid, we here make use of a small thin platinum cover, such as has been already described (§ 6), with the convex side placed downwards. The portions which have been melted with soda are next warmed, and evaporated to dryness with acetic acid before the addition of sulphuric acid. In this manner we prevent the loss which is caused by effervescence, while the fluoride remains intact; the acetic acid vapours which develop later on, during the distillation with sulphuric acid, are very favourable to the complete condensation of silicic fluoride. During the first half of the time necessary for the transformation of the fluorides into sulphates the matter must be kept warm; the drop of water which has served to cool the cover is removed, and the drop containing the fluoride is placed on a plate of varnished glass, or a polished plate of heavy spar, which answers the purpose better.

We can easily make plates of heavy spar suitable for this experiment by taking the pieces obtained by following the cleavage planes, about 1.5 to 2 c.m. long and 2 or 3 m.m. thick, and sticking them to plates of glass by means of Canadian balsam, so as to avoid the cracks which would ensue in the second cleavage plane; they are then rubbed on a very smooth oilstone, then with water, and after that with oil, and finally polished by rubbing with a piece of very soft leather and oxide of tin.

I use chloride of sodium as a reagent, and I put 1 or 2 m.grms. of the solid salt into the drop under examination. If the hydrofluosilicic acid is not too dilute, we first see forming elegant rosettes with six points, measuring about 100 microns; later on we notice the appearance of hexagonal tablets, and prisms combined with pyramids, of about 25 microns in length. They are slightly cloudy in appearance and of a delicate rose-colour.

The potassic fluosilicate is much less soluble, but much more difficult to recognise, on account of its extraordinary transparency.

By following this method exactly as has been described I have succeeded in obtaining satisfactory results with 0.0036 m.grm. of fluorine.

20. Test for Silicon and Boron.

The test for silicon and boron is conducted in the same manner as that for fluorine, the only difference being that in the first case we use hydrofluoric acid conjointly with sulphuric acid, and we can only use plates of varnished glass or a plate of heavy spar, while in the test for fluorine

we can in cases of necessity employ ordinary plates of glass.

The method of distillation is the same as in the case of fluorine (§ 19). We make use of sodic chloride as the reagent, when we only have to try for one of the two above-named elements; it gives, with hydrofluoboric acid, precisely the same hexagons and the same results as it does with hydrofluosilicic acid. The reaction enables us to detect with facility 0.08 m.grm. of silicic acid and 0.04 m.grm. of boric acid.

In the greater number of cases we have to try for boron when mixed with a preponderating quantity of silicon (axinite, datholite, tourmaline); in these cases chloride of sodium will not answer. After having made several unsuccessful attempts, I succeeded in finding two very distinctive reactions, which I will now give, for want of other more suitable means.

The solution of calcic fluosilicate, evaporated down until very concentrated, gives small lenticular-shaped masses, of about 20 microns in length; the fluoborate, under the same conditions, appears in the form of short rhombic prisms, which generally offer themselves to our view with their section transversal; the rhombs, which have tolerably sharp angles, are about 10 to 15 microns in length and 8 to 12 microns in width. The reaction is exceedingly useful when we do not have to deal with sulphuric acid at the same time as hydrofluoboric and hydrofluosilicic acids.

The potassic fluosilicate gives crystals belonging to the regular system. They are octahedra and cubes combined with octahedra; the potassic fluoborate appears, when the acid is sufficiently concentrated, under the form of narrow-pointed strips, and afterwards as rhombs, the length of whose diagonals are in the proportion of 2 : 3. Their length varies from 30 to 50 microns. The two obtuse angles are often truncated; sometimes, also, the larger crystals show indications of a truncated pyramid. The potassic fluoborate crystallises after the fluosilicate; it is necessary to pay attention to this fact when searching for boron in the presence of a large quantity of silicon.

If we were to add the potassic chloride immediately to the product obtained by the distillation with sulphuric and hydrofluoric acids, it is very possible that we should not perceive the fluoborate; in any case we should have some trouble in recognising the small number of these crystals amongst the large quantity of octahedra of potassic fluosilicate. I therefore recommend the elimination of the greater part of the silicon. To effect this we warm the mixture of the mineral with sulphuric and hydrofluoric acids for a space of time long enough to drive off the greater part of the silicic fluoride, which can be absorbed with water or dilute sulphuric acid, so as to enable us to test for hydrofluosilicic acid in the manner already described in § 19. We repeat the operation after the addition of a fresh quantity of hydrofluoric acid; we increase the temperature little by little until the vapour of sulphuric acid commences to come off, because the boiling-point of hydrofluoboric acid is almost as high as the boiling-point of sulphuric acid.

The product of the second distillation is heated up to 120° C.; after waiting a few minutes, a drop of water is added, and then the potassic chloride. If the rhombic crystals of potassic fluoborate do not show at once, it is not a proof of the absence of boron; we should in every case wait until the complete desiccation of the drop.

21. Test for Water.

In some special cases it may be very necessary to prove the presence of water in a very small specimen of the mineral. By proceeding carefully we can detect the presence of a tenth of a m.grm. of water by following a plan analogous to that employed in blowpipe analysis. The essential point in this method is to concentrate the small quantity of water into as small a space as possible,

and to prevent, at the same time, any loss of that present or the introduction of any water vapour from without.

For this purpose I employ tubes having an inside diameter of 2 m.m. and 10 c.m. long, drawn off to a fine point of 0.5 m.m. diameter and 2 c.m. long. After having warmed the tube from one end to the other, and having passed air through it, by sucking through an india-rubber tube attached to the other end, the fine end of the tube is sealed up in the lamp. The fragment of mineral is put in while the tube is still warm, and the tube is then sealed in the blowpipe about half-way along, taking care not to leave a fine end, and also not to allow any water vapour from the flame to find its way in. The fine end is then cooled by means of alcohol; and when we cannot observe any deposit of water there, we gently heat the other end, where the mineral is, up to dull redness.

Generally the water collects at the shoulder where the tube is drawn off, without it being necessary to cool it. By bringing the flame further along we can concentrate all the water in the capillary end.

To prove the presence of very small quantities of water we can still have recourse to a reaction which is based on the colouration of fuchsine under the influence of water. It is obvious that to effect this the tubes must be prepared beforehand.

An alcoholic solution of fuchsine leaves, by evaporation on a glass plate, a slight opaque film, of a yellowish green colour and a metallic lustre. If we introduce a narrow band or some particles of this substance into the capillary part of the tube, and if we then drive the deposit of condensed water towards the spot where the fuchsine is, we observe that the latter loses its metallic lustre and takes a transparent red colour.

(To be continued).

AN APPARATUS FOR MAINTAINING CONSTANT TEMPERATURES UP TO 600°.*

By G. H. BAILEY, D.Sc., Ph.D.,
Assistant Lecturer on Chemistry, The Owens College.

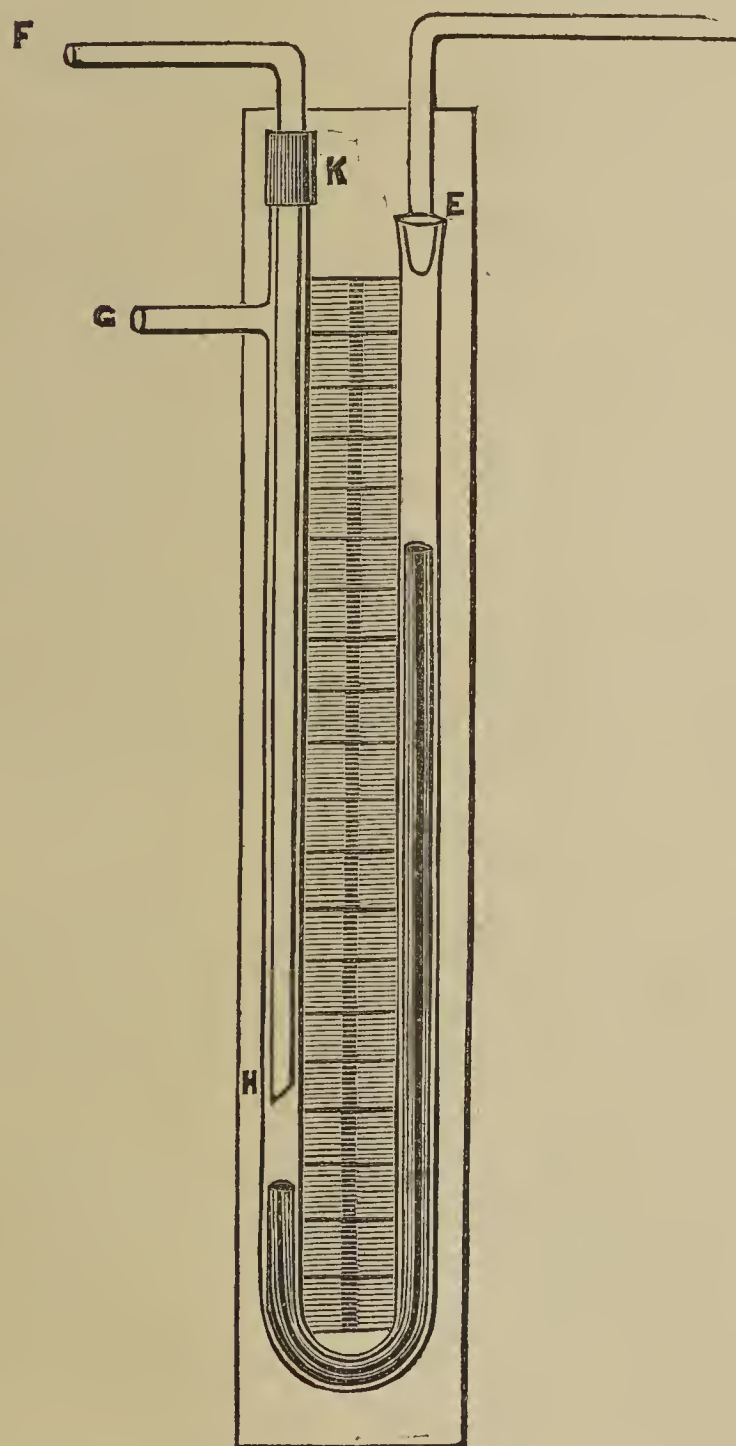
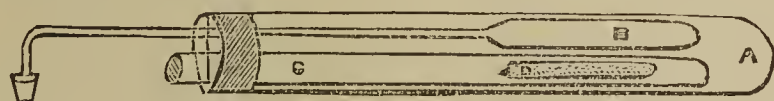
SEVERAL months ago this apparatus was described before the Chemical Society. It consists essentially of a furnace (not shown in the figure) of six Bunsen burners, a heating tube, an air thermometer (so arranged that the temperature may at any time be estimated), and a regulator by which the temperature may be limited and kept constant. These parts will be described in the order given.

The heating tube (A) is of combustion glass, closed at one end; it is 25 c.m. long and 4 c.m. in diameter, and is placed horizontally within an iron casing over the furnace. Within this is the heating tube proper (C), into which the substance to be heated is introduced in a platinum boat (D), whilst alongside this tube is the bulb (B) of the air thermometer.

In order that the temperature, as indicated by the air thermometer, may as nearly as possible correspond with that of the substance heated, the inner tube and air thermometer are arranged along the horizontal diameter of the outer tube, and this latter is separated from the iron casing by an air space. In point of fact it is found that the variations of temperature do not exceed 2 or 3 degrees. The bulb of the thermometer is connected, by means of a capillary tube, with a U-tube (E), the near limb of which is in the first instance filled with mercury, whilst the further limb contains a column of 3 or 4 c.m. As the heating proceeds the column of mercury in the near limb of the U-tube is depressed, the amount of the depression being a measure of the temperature; indeed the instrument may be graduated by noting the temperature on a high-boiling thermometer placed in the heating

* A Paper read before the British Association, Birmingham Meeting, Section B.

tube, and the reading of the mercury column on the millimetre scale attached to the U-tube. The further limb of the U-tube answers as regulator, and by it we are enabled to limit the temperature to any desired degree. This is done by causing the gas supply for the furnace to pass through the tube (F, H) and out at the side tube (G). At H the tube is cut off slantwise, and perforated with a small hole a little above the outlet, as in an ordinary gas-regulator. As, then, the column of mercury is depressed in the near limb of the U-tube, it rises in the further limb, ultimately reaching the outlet (H) and partially cutting off the gas supply; it is evident, therefore, that if the



NOTE.—The upper figure is drawn to only half the scale of the lower.

outlet of the regulator is only a short distance above the mercury, this point is soon reached, and a low limit of temperature (say 100°) is attained. The temperature can be kept at this point for any period desired; then by raising the regulator somewhat (and this is easily done, since it slides in the indiarubber connection, K) a higher limit (say 120°) can be attained, and so on up to 600°, beyond which no trial of the apparatus has been made.

In order to prove that the apparatus is reliable the author has determined a number of melting-points with it; he has also calculated the temperatures from the

known volume of the air-thermometer bulb, according to the law of expansion of gases.

An attempt to control the higher temperatures by Siemens's electrical method, though it showed general agreement, cannot be said to have confirmed the observations with any definiteness, since in this method so much depends on the particular character of the platinum used.

The immediate purpose for which the apparatus was designed is the determination of the atomic weight of those elements in which it is necessary to employ the normal sulphate, and the author is of opinion that by the use of such means the determination from the sulphate may attain a much higher degree of accuracy than heretofore. The normal sulphate will be heated at successive temperatures until decomposition begins to set in, this point being indicated by aspirating a current of air through the heating tube after each period, and passing it through a solution of barium chloride. Having determined the lowest temperature at which decomposition occurs, the sulphate is then heated with excess of sulphuric acid, and that point determined at which it loses all free sulphuric acid; and these temperatures having been ascertained once for all, it is only necessary in further experiments to heat the sulphate (with excess of sulphuric acid) at some temperature lying between these limits until constant.

As the process can be watched and the products of decomposition collected and examined, it is hoped that the apparatus may prove useful in examining the general phenomena of decomposition of salts by heat.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 292.)

DR. GASCOYNE then read the following experiments designed to compare the official method for determining total phosphoric acid by ignition with magnesium nitrate with that of dissolving in nitric acid without previous ignition:—

Samples of commercial fertilisers containing large percentages of organic matter derived from fish scraps, tankage, azolin, &c., were used in the experiments.

In the nitric acid method 2 grms. of the fertiliser were dissolved in 50 c.c. nitric acid and a few drops of hydrochloric acid, the solution made up to 1 litre, and an aliquot taken representing $\frac{1}{2}$ gram. of the material.

					Official method.	Nitric acid method.
No. 1, commercial fertiliser	11.64	11.66
No. 2, commercial fertiliser	10.15	10.12
No. 3, commercial fertiliser	12.01	12.08
No. 4, commercial fertiliser	11.05	11.01
No. 5, commercial fertiliser	12.86	12.77
No. 6, commercial fertiliser	11.90	11.93
No. 7, tankage	13.65	13.68
No. 8. bone meal	23.27	23.26
No. 9, fish scrap	7.17	7.22
No. 10, tankage	9.19	9.16

It will be seen that the nitric acid method is quite as satisfactory as the official.

The Secretary then read, by consent of the Association, a paper contributed by Dr. William Frear and H. B. McDonnell, of the State College of Pennsylvania, entitled:—

A Comparison of Wagner's and the present Association Methods for the Determination of Available Phosphoric Acid.

Some time ago the fertiliser control stations of Southern Germany adopted for their official method for the deter-

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

Designation.	Association Method.					Wagner's Method	
	Total P_2O_5 .	Soluble.	Insoluble.	Reverted.	Available.	Soluble.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	a. Per cent.	b. Per cent.
1. Fine ground South Carolina rock	27.11	0.00	25.85	1.26	1.26	1.56	1.37
2. Fine ground apatite	39.44	0.00	38.59	0.85	0.85	0.66	0.63
3. Fine ground bone	24.06	0.16	19.33	4.57	4.73	5.19	5.28
4. Dissolved South Carolina rock ..	17.19	10.04	3.50	3.65	13.69	11.56	11.49
5. Dissolved bone-black	16.02	12.32	0.66	3.04	15.36	15.24	14.80
6. Dicalcium phosphate	43.76	3.77	11.85	28.14	31.91	23.67	23.44
7. Dissolved bone-ash	21.87	14.29	3.61	3.72	18.01	14.39	14.74
8. Raw Navassa	28.83	0.00	27.80	1.03	1.03	2.42	2.51
9. Orchilla guana	18.11	0.00	14.43	3.69	3.69	3.25	3.27

mination of available phosphoric acid, that employing an acid solution of citrate of ammonium, as proposed by Prof. P. Wagner. This method, together with an abstract of the results obtained by Wagner in the treatment of various phosphates, was presented by Dr. Shepherd in a late number of the *American Chemical Journal*, to which I will refer for the details of the method.

At my suggestion a comparison of this method with that at present approved by the Association of Official Agricultural Chemists was made by Mr. H. B. McDonnell in the laboratory of the Pennsylvania State College.

The results of his analyses of various phosphatic substances are presented in the appended table.

In determining Wagner's "soluble" acid (corresponding to our "available") duplicates of samples 1a to 6a were taken from different flasks, which stood about twenty hours over night, and were frequently shaken during the afternoon and morning. Samples 1b to 6b were treated similarly, but stood only six hours. The duplicates of 7a to 9a were taken from the same flasks and stood fourteen hours; 7b to 9b stood sixteen hours.

Owing to the pressure of other work, I am unable to do more than note the facts most clearly shown by the data.

Accepting the means of the results of 1a to 6a and 7b to 9b as those best representing Wagner's method, a comparison with the "available" acid obtained by the Association method shows that the former method gives somewhat higher results with fine ground South Carolina rock and fine ground bone, and more than doubles the amount in raw Navassa rock. On the other hand, it gives somewhat lower results with fine ground apatite, dissolved bone-black, and Orchilla guano, and several per cent less with dissolved South Carolina rock, dissolved bone-ash, and dicalcium phosphate.

A comparison of the results in columns a and b to determine the limits of time in which the solution is completed, taking first samples 1a to 6a, shows that sixteen hours suffices to practically complete the solution of the available acid in fine ground apatite, fine ground bone, and dissolved South Carolina rock; and that there is a gain of 0.1 to 0.4 per cent by standing twenty hours in the other cases. In samples 7 to 9 the results with Orchilla guano are not materially aided by an increase of two hours over the original fourteen hours allowed for solution, but in the other cases the gain is considerable.

The President then announced the subject as open to discussion.

Mr. CHAZAL remarked upon the uncertainty of determining specific gravity by means of the densimeter, except when great care is used in correcting the instrument, and hoped the determination by weight would be recommended.

Professors MOSES and LUPTON thought that the densimeter should be retained as a matter of convenience, but that careful correction should be made upon the instruments used.

Dr. JENKINS called attention to the fact that new thermometers of approved make are occasionally incorrectly graduated, and a thermometer, correct, when new, will, on use, change its zero point very considerably, so that frequent examination is necessary to secure exactness as to temperature, both in the preparation of ammonium citrate and in the extraction of citrate-soluble P_2O_5 .

Prof. JOHN A. MYERS remarked that it is possible that much of the variation in the results of analysis may, no doubt, be accounted for by the fact that weights and other instruments used in the processes of analysis are subject to wide variations. Out of eight sets of weights in his laboratory bought for standard sets but three sets could be found that would compare sufficiently closely not to seriously affect the results of the work. Whether this trouble extends to other laboratories in the country he had no means of ascertaining.

The possible effects in the variation in the thermometers, and also in apparatus for determining specific gravity, may be seen in the difficulty of getting concordant results in our insoluble phosphate determinations, thus affecting the citrate of ammonium solution appreciably.

The opinion was finally elicited that members should use the methods which they preferred, but that great care should be used to insure accuracy.

Mr. CHAZAL then called attention to the loss occasioned when, in washing out soluble phosphoric acid, the fertiliser is washed from the funnel into a mortar and returned to the filter; also to the disadvantage of shredding filter-paper into citrate solution, causing danger of imperfect washing out with water, and also retarding contact of fertiliser with the citrate solution when shaken.

He also brought up the question of the use of magnesian nitrate, and showed the possibility of the retention of phosphoric acid in the hard white cake formed on ignition.

Dr. WHITE then read some notes of experiments on the use of $Mg(NO_3)_2$ in ignition.

On the Use of Magnesium Nitrate.

The following experiments were made to determine if ignition with $Mg(NO_3)_2$, in order to destroy organic matter, could be replaced by wet methods:—

(1) A commercial fertiliser containing acid phosphate, potash salts, and animal matter, was selected; total P_2O_5 was determined.

(a) By digesting 0.5 gm. for thirty minutes with 30 c.c. concentrated HCl.

(b) By digesting 0.5 gm. for thirty minutes with 30 c.c. concentrated HCl, adding at intervals pinches of finely-powdered $KClO_3$ (0.5 gm. in all).

(c) By digesting 0.5 gm. for thirty minutes with 30 c.c. fuming HNO_3 .

(d) By igniting 0.5 gm. with $Mg(NO_3)_2$ in usual manner.

Results were as follows:—

	a.	b.	c.	d.
Total P_2O_5 ..	{ 11.68 11.73	{ 11.95 11.98	{ 11.82 11.80	{ 12.05 11.93
Mean	11.70	11.97	11.81	11.99

(2) A commercial fertiliser containing acid phosphate, potash salts, and cotton seed meal was selected. Methods detailed above were employed. Results were as follows:—

	a.	b.	c.	d.
Total P_2O_5 ..	{ 10.12 10.28	{ 10.52 10.54	{ 10.36 10.32	{ 10.47 10.47
Mean	10.20	10.53	10.34	10.47

The results showed that the use of KClO_3 with HCl was much the best method of working, both in convenience and results.

The general testimony which followed was in favour of oxidation of the organic matter in other ways than by means of $\text{Mg}(\text{NO}_3)_2$.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

December 11th, 1886.

Prof. H. McLEOD, F.R.S., Vice-President, in the Chair.

W. NATANSON, E. Natanson, the Hon. R. Abercromby, Jul. Verteimer, and H. M. Elder were elected Members of the Society.

The following papers were then read:—

“On the Influence of Change of Condition from the Liquid to the Solid State on Vapour Pressure.” By Prof. W. RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.; read by Dr. YOUNG.

The authors refer to some experiments published in Wiedemann's *Annalen* (vol. xxviii., p. 400), by W. Fischer, on the above subject, which show that the vapour pressure of ice and solid benzene are less than those of water and liquid benzene at the same temperatures. By using the formula $p = a + bt + ct^2$ to express the relation between the pressure and temperature of saturated vapours, Fischer arrives at the absurd result that the vapour pressure of liquid benzene is not identical with that of solid benzene at its melting-point. If the above formula be replaced by $\log p = a + b a^t$, it is shown that the anomaly disappears. The authors have measured the vapour pressures of solid and liquid benzene by the dynamical method, and obtain results agreeing closely with those of Fischer determined statically. They also calculate the vapour pressure of solid benzene from that of the liquid, using the formula—

$$P_{t-1} = P_t - (P'_t - P_{t-1}) \left(\frac{V_{t-\frac{1}{2}} + F_{t-\frac{1}{2}}}{V_{t-\frac{1}{2}}} \right),$$

where P_t and P'_t are the vapour pressures of the solid and liquid at temperature t , $V_{t-\frac{1}{2}}$ = heat of vaporisation of liquid, and $F_{t-\frac{1}{2}}$ = heat of fusion of solid at temperature $t - \frac{1}{2}$. The numbers so obtained are in accordance with those determined experimentally.

“On the Nature of Liquids as shown by the Thermal Properties of Stable and Dissociable Bodies.” By the same Authors; read by Prof. RAMSAY.

From experiments on the vapour density and heat of vaporisation of stable and dissociable bodies the authors arrive at two important results:—(1.) That for stable bodies such as alcohol and ether the density of their saturated vapours increases with rise of temperature, whereas for bodies such as acetic acid and nitric peroxide the vapour density attains a minimum at a certain temperature and increases with either rise or fall of temperature. (2.) The heat of vaporisation of alcohol decreases with rise of temperature, but that of acetic acid attains a maximum at about 110°C . and decreases with rise or fall of temperature. From these results the authors seek to prove that the difference between stable liquids and their vapours consists in the relative proximity of the molecules, this proximity being greater in liquids than gases, and that the molecules of stable liquids are not more complex than those of their gases.

Prof. PICKERING dissented from this view, and thought that the molecules of liquids are aggregations or compounds of those of the gases.

In answer to enquiries by the authors, Mr. LEWIS WRIGHT said bodies which rotate the plane of polarisation of light when in the liquid state also rotate it in a proportionate degree when gaseous; and Captain ABNEY remarked that stable liquids and their vapours give similar absorption spectra, whereas those of dissociable bodies differ considerably. Both these facts seem to support the view put forward by the authors.

An Account of Cauchy's Theory of Reflection and Refraction of Light. by JAMES WALKER, M.A.

This paper is intended as a statement of the work previously done in the subject, and gives references to the original papers and “reproductions,” &c., which will be of great value to persons studying this important branch of the theory of Optics.

Mr. SHELFORD BIDWELL exhibited and described a voltaic cell in which the electrolyte is dry peroxide of lead. It consists of carefully dried peroxide placed between plates of lead and sodium, and gives a comparatively strong current, which passes from the sodium to the lead within the cell.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, November 2nd, 1886.

Professor OSBORNE REYNOLDS, LL.D., F.R.S., Vice-President, in the Chair.

“The Action of Hydrochloric Acid Gas upon certain Metals,” by J. B. COHEN, Ph.D., F.C.S. Communicated by Dr. A. SCHUSTER, F.R.S.

From certain considerations I was led to believe that hydrochloric acid gas, freed from all traces of water, would not act upon certain of the metals. This idea was further supported by the observations of Gore with liquefied hydrochloric acid (*Proc. Roy. Soc.*, xiv., p. 204), who found that zinc, iron, &c., were scarcely acted upon, and that out of fifteen metals, only one, viz., aluminium, was dissolved by the pure liquefied acid.

Preparation of Dry Hydrochloric Acid Gas.—The gas was prepared by the action of ordinary concentrated sulphuric acid, previously well boiled, upon lumps of fused sodium chloride. The gas passed through two wash-bottles containing concentrated sulphuric acid (previously boiled), then through a series of eleven bulbs blown on one stem, and placed at an angle of about 45° , also containing concentrated sulphuric acid; and, finally, through a tube about twenty-six inches long and one inch wide, well packed with phosphoric anhydride. The evolution flask was connected by a T piece, with the drying apparatus on the one hand and with a tube dipping under dry mercury on the other, the latter serving as a safety valve. All the joints were well secured with thick india-rubber tubing, wrapped round with copper wire, and then thickly coated with melted paraffin.

The first metal experimented upon was metallic sodium.

Preparation of Metallic Sodium.—The following method was found to give the best results in preparing clean metallic sodium. It is one, however, which requires the exercise of patience, because often as many as a dozen of the tubes employed break before a successful operation is achieved. A clean glass tube, about $1\frac{1}{4}$ feet long and $\frac{3}{4}$ inch diameter, is drawn out at one end into a pear-shaped bulb. This is placed vertically in a clamp with the pear-shaped bulb downwards. This may be called the bulb end. Through the bulb end a current of coal-gas is passed until most of the air is displaced. A plug of glass-wool is meanwhile introduced through the upper end so as to fall over the constricted part of the tube, and above this pieces of clean dry sodium are placed so as to fill about one-half of the upper portion of the tube. The tube is

then closed at the upper end with a cork and sealed at the lower end before removing the connection with the coal-gas delivery tube. The cylindrical part is now sealed. There still remains in the tube a considerable quantity of air. To absorb this, the sodium is melted at a gentle heat over the flame, allowed to cool, and the operation performed repeatedly for two or three days, the tube being held in a horizontal position. The sodium is now filtered through the glass-wool into the pear-shaped bulb. This is done as follows:—The sodium is first melted and the tube tilted with the bulb end downwards. On heating the bulb, bubbles of gas are driven through the melted sodium, and on cooling, the tube being still held vertically, the sodium passes slowly into the bulb through the glass-wool, which retains the unmelted oxide. This process of filtration may be hastened by warming at the same time the upper part of the tube. If sufficient time has been allowed, and the re-melting of the sodium often enough repeated, the metal runs through and has a bright metallic surface. Out of a large number of tubes prepared in this way only two were successful. The glass easily cracks on warming the metal when firmly adhering to the walls. The pear-shaped bulb is now sealed off and the sealed ends doubled round in the form of hooks. The bulb is placed in one compartment of a tube drawn out in the middle; the other compartment is filled with phosphoric anhydride and separated by a plug of glass-wool. This tube is connected with the hydrochloric acid apparatus, the compartment containing the bulb being attached to the phosphoric acid tube of the hydrochloric acid apparatus. The other end is connected with a wash-bottle of concentrated sulphuric acid. All the joints having been carefully secured, hydrochloric acid gas is slowly bubbled through the apparatus for several hours (both before and after attaching the sodium tube) until a sample of gas issuing from the last wash-bottle is entirely absorbed in water. The tube containing the sodium is also heated gently whilst the gas is passing through to drive off traces of moisture possibly adhering to the sides. The sodium tube is now sealed off at both ends, and the bulb broken by allowing the hooked ends to fall sharply against the end of the tube. The following results were then noted in two experiments:—

1. The sodium retained its metallic appearance for a few weeks, and it slowly assumed a dark grey colour, finally, after several months, a deeper violet grey.

2. The sodium lost its metallic appearance much more quickly, and after a few weeks became dull black, like charcoal. This blackness did not extend far below the surface, that portion of the metal attached to the glass retained its mirror-like appearance.

The composition of this black compound has not been further investigated; but it may possibly be a sub-chloride of sodium.

Experiments with metallic aluminium point to the fact that it is unacted upon by the gas when dry, whereas, as is well known, it is readily tarnished by moist hydrochloric acid gas, and dissolves in the liquefied acid.

These experiments, which have for the present been discontinued owing to want of time, will be taken up again, and a large number of facts, if possible, collected.

"*Capillary Constants of Benzene and its Homologues occurring in Coal-Tar*," by J. B. COHEN, Ph.D., F.C.S. Communicated by Dr. A. SCHUSTER, F.R.S.

The object of the present paper is to bring before you a subject which promises to have special interest to the chemist, viz., capillarity as a property on which a method of analysis may be based. Capillary constants of liquids, and their relation to chemical composition and constitution, have been recently carefully studied by Schiff, who determined these constants at the boiling temperatures of the liquids. More recently, Traube has investigated the constants of substances in solution, a practical outcome of which has been a method for determining the percentage of fusel oil in spirits and wines. This method is fully given in the *Berlin Berichte*,

xix., 892, and the apparatus described in the *Journ. f. Prakt. Ch.* (2), xxxi., 177. Wishing to extend this method, and simplify it, if possible, for practical purposes of rapid analysis, I undertook the determination of the capillary constants of benzene and those homologues of benzene which occur in coal-tar. The reason for attacking this special line was simply because, as those who are acquainted with the coal-tar industry know, the methods at present in use for determining the percentage constituents of benzene and its homologues occurring in commercial coal-tar naphtha are rough methods, and lack accuracy; and there is, especially, no quick method for determining the presence and estimating quantitatively carbon-bisulphide, paraffin, or petroleum, which are often found in the commercial products. In these determinations I must admit, at the outset, that no very great success has attended them; at the same time, the value of the method should not be overlooked; and, as to the results, I have very little doubt that those who care to pursue the subject will hit upon something which will turn out more useful and successful—for example, in the analysis of mixtures of oils. To fulfil the conditions of a practical analytical method, the apparatus must be of simple construction, easily manipulated, and the determination rapidly performed, consistent, of course, with accuracy. For comparative determinations, the apparatus to be described will be found to answer well. Instead of using a capillary with a movable and adjustable scale employed by Traube, I find that a piece of thick thermometer tubing, with a fine round capillary, 0.155 m.m. bore and about 26 c.m. long, which was supplied to me by Mr. L. Casella, of London, served my purpose excellently. Along its whole length it was etched in millimetres. By a very simple arrangement of a mirror, usually used in such determinations, it is a matter of little practice only to be able to read off the scale to tenths of a millimetre with a pocket magnifying glass.

The first point to be determined before employing this tube was, whether a piece of thermometer tubing, 0.155 m.m. bore, could be thoroughly cleaned and dried without deteriorating with use. The tube was thoroughly cleaned with ether or alcohol after each determination, by plunging it half way in pure dry ether, so that the ether rose at least two-thirds of the distance up the capillary. By bringing the lower end on to a piece of clean silk cloth, the capillary was rapidly emptied, and this process repeated three or four times, and finally dried by the following arrangement:—The thermometer tube is placed in an outer tube of glass, closed at one end and constricted in two places. At the open end of the outer tube a plug of cotton-wool is inserted round the thermometer tube, which serves to filter the air passing into it. The thermometer tube is attached by a piece of india-rubber tubing to a narrow glass tube containing cotton-wool; and by a longer piece of india-rubber to a calcium chloride tube, which may be closed by the pinch-cock and india-rubber tube. The glass tube, which is perfectly cleaned before use, is plugged with cotton-wool when not required. In order to dry the capillary, the apparatus is fitted up as described, and the outer tube heated. By partly exhausting the air at the pinch-cock end, which is then tightly closed, a partial vacuum is produced, and with my tube the pressure equalised itself after about six minutes, during which time a constant stream of hot air was passing through the capillary. With such an arrangement, and by always taking the precaution to cover the thermometer tube, whilst in use, with an open glass cap containing cotton-wool, I found that a tube of this kind might be employed for an almost unlimited number of determinations. These determinations were made in the following manner:—The liquid was placed in a small bottle; the thermometer tube, after being sunk into the liquid and adjusted perpendicularly by a plumb-line, was left for a short time. The height to which the liquid had risen was read off on the scale in millimetres with a magnifying glass, and the reading below the meniscus also taken. The

difference gives the height in millimetres which the liquid has risen in the capillary. The tube is now raised a few millimetres, and the height again read off; the process repeated once or twice and the mean height taken. With pure benzene, the following gives the height in millimetres of the column of liquid, determined at different times in the course of the present investigations:—

	Height in millimetres.	Temp.
1.	83.65	15°
2.	83.4	15°
3.	83.05	16°
4.	83.05	16°

As is well known, in such determinations the temperature is a very important factor. As in the case just given, 1° C. corresponds to a difference of about 0.05 c.m. I therefore carefully noted the temperature of the room at the beginning of each reading, and took care to leave all the vessels and liquids there several hours before use. During the whole time the temperature remained between 15° and 16°. No precaution against evaporation was taken nor required, except in the case of mixtures, when a plug of cotton-wool was inserted in the neck of the bottle. The mixtures were made by running in from a burette a certain number of drops of the different liquids.

	Boiling-point.	Height in m.m.	Temp.
Benzene	80—80½	{ 83.65 83.05	{ 15° 16
Toluene	109.7—110.05	{ 83.95 83.2	{ 15 16
Orthoxylene ..	143.8	86.95	15½
Paraxylene ..	137.6—138.8	83.80	15½
Metaxylene ..	138.2—138.7	84.3	16
Pseudocumene..	167—169	86.1	16
Mesitylene ..	160—161	84.75	16
Alcohol (absolute)	71.5	—
200 drops benzene	{ 82.5	{ 16
2 „ alcohol		
Carbon bisulphide	64.9	15
200 drops benzene	{ 82.7	{ 15
5 „ CS ₂		
200 drops benzene	{ 81.45	{ 15
10 „ CS ₂		
Petroleum	79—81	71.8	15
300 drops benzene	{ 82.45	{ 15
10 „ petroleum..		
300 drops benzene	{ 83.1	{ 15
6 „ petroleum..		

It appears from the above that in the case of the pure hydrocarbons the difference is too small to be able to base upon it any reliable method of analysis. In case, however, of small quantities of impurities, which are often found in commercial benzene, the height of the column is sufficiently depressed to be able to detect the presence of small quantities of carbon bisulphide or petroleum.

NOTICES OF BOOKS.

Outlines of Quantitative Analysis. By A. HUMBOLDT SEXTON, Professor of Chemistry in the College of Science and Arts, Glasgow. London: Charles Griffin and Co.

THE author, in his Preface, points to a very important object at which his book is aiming. "To the practical man it [*i.e.*, the study of actual quantitative work] is also of great value; not that it will enable him to dispense with the services of the professional chemist, but—and this is more important—it will enable him to understand the meaning and the value of analytical results,—a know-

ledge which is unfortunately not very common among practical men." Too true: the consulting chemist is sometimes expected to effect things absolutely self-contradictory,—*e.g.*, to increase the percentage of one ingredient in a compound without diminishing that of the others.

Mr. Sexton gives one method only for each determination,—a limitation perfectly justifiable in a book of such limited extent.

After a preliminary account of the balance he gives a chapter of introductory exercises, such as determinations of moisture, of ash, of solid matter in solutions, of the specific gravity of liquids, and of insoluble matter in salts. He then proceeds to simple gravimetric analyses, one substance only being determined in each case.

Then follow exercises in volumetric analysis, beginning with alkalimetry and acidimetry. Here we notice that litmus is the only indicator recommended.

In the chapter on determinations with previous separation, the method given for separating alumina from iron is the alkaline hydrate process, whilst for separating cobalt and nickel the author uses the potassium nitrite.

Then follow miscellaneous examples, varying much in their difficulty, and consequently in the degree of skill and care which they require.

Lastly, we find instructions for ultimate organic analysis and Appendix of Tables.

The various processes are carefully described, and the student is warned against possible sources of error.

Organic Colouring-Matters (Organische Farbstoffe). By Dr. R. NIETZKI. Breslau: Eduard Trewendt.

THIS work is a separate re-publication from the chemical department of the "Encyklopædia der Natur Wissenschaften," now being issued by the above-named publisher.

In his very interesting Introduction the author contends that the compounds formed by organic fibres with colouring-matters are compounds analogous to salts, in which the fibre plays the part sometimes of an acid and sometimes of a base. Thus if we introduce woollen or silk into the colourless solution of the rosaniline, the fibre is dyed intensely red, just as if a corresponding quantity of a salt of rosaniline had been present. To explain this phenomenon, the author considers that the colourless base forms with the fibre a compound which behaves like a salt of rosaniline. Hence in this compound the fibre plays the part of an acid. "Salts of colour bases are probably decomposed by the process of dyeing,—at least this assumption explains the fact that certain very strongly basic colours, in the form of salts, do not take upon wool. Such a colouring-matter is, for instance, methyl-green. Its salts, like all those of the ammonium bases, are very stable, and woollen yarn introduced cannot decompose them, and hence it remains not dyed. The dyeing, however, takes place if the bath is rendered slightly alkaline by the introduction of ammonia. The silk fibre seems to have more decidedly acid properties than that of wool, and it is therefore dyed also by colours of the kind just mentioned. Corresponding phenomena are encountered in dyeing with acid colouring-matters. The animal fibre is generally unable to decompose the salts of tinctorial acids, and the latter must be set at liberty by the addition of other acids."

This would explain why the woollen-dyer finds an addition of sulphuric acid to his dye-pans so often necessary.

The author fully admits the difficulty of explaining, from a chemical point of view, the exceptional affinity of curcumine and carthamine for vegetable fibres. His views, however, widely as they differ from the prevalent theory of the process of dyeing, seem to us to merit a careful experimental investigation.

Dr. Nietzki divides the organic colouring-matters into two great classes, the natural and the artificial. From the former he excludes, however, alizarine and indigo. In

the former case we must agree with him, since probably all the alizarine of commerce is obtained artificially. As regards indigo we must demur. Very lately Dr. O. Witt, who, as a German, would naturally sympathise with the attempt to produce indigo-blue in German manufactories instead of in Indo-British plantations, frankly pronounced artificial indigo a chemical curiosity, and owned that, as far as practical purposes were concerned, the plant must retain its supremacy.

Among the natural dyes we find no mention of the colouring-matter of bar- and cam-woods, though santaline—the colouring-matter of santal-wood—is duly described.

Flavine is not mentioned under quercitron-bark, nor do we find any notice of fustine, the colouring-matter of the so-called young fustic.

Orchil is much more commonly used as a paste than as a powder.

Xylindene is a very curious green colouring-matter, which might be of practical value if it were more abundant. It is found sometimes in the decaying wood of the beech, oak, and hirsch.

Berberine receives notice as the only natural colouring-matter of a basic character. It behaves with the fibre like the artificial basic dyes, and is fixed upon cotton by means of tannin.

In speaking of carmine the author seems not to accept certain recent investigations, which show that this pigment contains not merely alumina, but lime, in such a state of combination as to be soluble in ammonia.

The classification of the coal-tar colours is admitted to be a task of no small difficulty. The arrangement which he adopts is as follows:—Nitro-compounds; azo-dyes; triphenylmethan dyes: indamines and indophenols; safranines and their allies; aniline black; indulines and nigrosines; chinoline and acridine colouring-matters, and anthraquinone dyes. The number of compounds mentioned under these heads is very great, though a large part of them do not admit of any practical applications in the tinctorial arts.

Under each section there is a fairly complete bibliography of the subject.

Typographical errors in proper names have not in all cases been avoided. Thus the firm "Williams, Thomas, and Dower" is rendered William Thomas in (*anglicé* of) Dower, as if Dower were the name of some place where the above firm carried on their business.

Under "Aniline Black" we find no mention of a name which has of late become a household word among French and Belgian dyers in connection with patent litigation.

The account of Turkey-reds might be misunderstood to imply that the so-called alizarine oil (produced by the action of sulphuric acid upon castor oil) has superseded the emulsive olive oils, known in France as *huile tournante*.

This work compresses a wonderful quantity of information into the brief compass of 160 pages, and will prove a useful addition to the library of the colour chemist. A good index, however, would greatly enhance its value.

Notes on the Literature of Explosives. No. IX. By Prof. CHARLES E. MUNROE, U.S.N.A. (Reprinted from No. 35 of the *Proceeding of U.S. Naval Institute*).

THE author first gives a short account of the blowing up of the Flood Rock, which was successfully accomplished on the 10th October, 1885. The rock consisted of hornblende gneiss with intersecting cross veins, and it was thoroughly honeycombed with tunnels until they amounted to about 4 miles in total length. 80,000 cubic feet of rock having been removed, the walls and ceilings of these tunnels were then drilled with holes, and upwards of two hundred and eighty-eight thousand pounds of rackarock and dynamite cartridges placed therein; the explosion, which was effected by electrical means, lasted about thirty seconds. The rate of transmission of the terrestrial and aerial shocks was observed, but has not yet been reduced.

The next note is taken from an article by Gen. H. L. Abbot on "Recent Progress in High Explosives and their Uses in War," in which the question of using dynamite and gun-cotton in shells is discussed; such shells do not appear to be so destructive to a body of men as similar shells charged with gunpowder would be, because the action of dynamite, &c., when exploded, is intensely local; the object which artillerymen are endeavouring to accomplish is the destruction of armour plates by embedding a shell in the plate first, and then causing the explosion by means of a time fuse; but the difficulty appears to be in getting a moderate sized shell to carry a sufficient charge. The author then goes on to consider whether it would not be better to send a projectile with a much greater velocity and a less charge, but he concludes that this cannot be satisfactorily determined without experiments.

In some experiments for rendering the lighter petroleum oils inexplorable, the author found that if camphor were dissolved in kerosene, the flashing-point was raised 12°, but that, on the other hand, the vapour of this camphorated kerosene, when mixed with air, exploded with greater readiness than the original kerosene.

A note from the *Times* gives a description of a new explosive called hellhoffite, a solution of a nitrated organic compound such as naphthalene, phenol, or benzene, in fuming nitric acid. In the trials of this against other explosives, the charge of about 20 grms. was placed in a glass bottle, on the top of a truncated cone of lead 6 c.m. high and 4 c.m. diameter at the middle. The explosion of gunpowder caused no change; that of nitroglycerin compressed the cone about one quarter of its weight; while that of hellhoffite almost destroyed the cone, more than half of it being torn away, while the rest was very much defaced. Hellhoffite cannot be exploded by a lighted match or by concussion, both of which are great advantages.

A curious explosion is recorded in the *Boston Journal* of June 30, 1885. A gentleman had some chlorate of potash lozenges in his pocket, and, on returning his watch to his pocket one day, he was much startled and slightly burnt by the lozenges exploding; this explosion was evidently caused by concussion, and manufacturers are warned to avoid trituration and pressure when making these tablets.

Mr. Munroe, proposes to continue the publication of these most interesting Notes from time to time, and he invites authors, publishers, and manufacturers to send him copies of their papers and circulars, so that his notes may be as complete as possible.

Proceedings of the Illinois Pharmaceutical Association at its Seventh Annual Meeting, held at Rockford. Edited by ALBERT E. EBERT. Chicago, 1886.

THE first sitting was on Tuesday afternoon, June 8th, and after the Society had been welcomed by the Mayor of Rockford the President delivered his Address, in which, after reviewing the work of the Association for the past eight months, he condemned patent medicines as "the most gigantic fraud and worst evil scientific pharmacy has to deal with at the present time," and held out hopes that before long the Pharmacy Law would be modified so that the sale of these nostrums could be controlled.

The sale of patent medicines in America is carried on to a much greater extent than it is in England, although it has been increasing considerably with us during the past few years; but we do not see what steps could be taken to prevent the sale of any preparation that is not actually poisonous.

At the following meetings the Reports of several Committees were read and discussed.

In the latter part of this Report we find the answers which have been sent to queries set at the previous meeting. These queries are thirty in number. The first is as follows:—What drugs and preparations are prescribed by physicians in Illinois? Twenty-two answers

were received, each giving a thousand prescriptions, and they have been tabulated by the Secretary, Mr. L. Hogan, who finds that the number of substances required for the treatment of disease is being constantly augmented, and he concludes that we are either progressing very fast, or else there is a great deal of experimenting going on. The other questions cover a good deal of ground and seem to be very useful, inasmuch as the opinions of the different members can in this manner be learnt by all, much better than by discussion at the meeting.

CORRESPONDENCE.

THE TEACHING OF SCIENCE IN SCHOOLS.

To the Editor of the Chemical News.

SIR,—I was greatly struck with the quotation from Sir James Paget's speech (CHEMICAL NEWS, vol. liv., p. 296). Of many causes which render Science Teaching in Schools futile the following are well known:—

1. The head-master of most important schools are classical men.
2. Laymen, though sometimes fairly well qualified to teach Science, are thought good enough for most schools.
3. Head-masters frequently expect Science-masters to teach other branches, as (say) Mathematics, English, &c.
4. No time is given for preparation of class experiments, or the many necessary duties falling upon those who even have to teach but Elementary Science.
5. In most cases anything approaching research is out of the question.
6. Head-masters, many of whom are uniquely ignorant of the merest rudiments of Science, imagine that a man can go into a lecture-room and give a lesson—say in Chemistry—as one would take a class in Latin.
7. In fitted Laboratories want of space, time, and necessary appliances preclude the teaching of *real* Science, added to which fact the many examinations encourage what Prof. Armstrong calls "test-tubing" (as far as Chemistry is concerned).
8. The marks for Science Subjects, in examinations for public appointments, are very unfairly allotted, causing head-masters and parents to look askance at such subjects as Chemistry, Geology, &c.
9. In many cases the most intelligent pupils never have time for good Science work, so great is the importance attached to literary subjects, whereas the dullard and ne'er-do-well is relegated to the "Lab." just to amuse himself.

I hope the subject started in your paper may be opened up by men far better qualified to write than myself.—I am, &c.,

J. H. B.

AN EXAMINATION PUZZLE.

To the Editor of the Chemical News.

SIR,—May I beg for space to point out that your correspondent A. P. S. (CHEMICAL NEWS, vol. liv., p. 297) has left unexplained the most serious part of the misconduct of *x* (p. 273), which was charged with giving no precipitate with *platinum chloride* after filtration from a precipitate produced by *ammonia*.

Sodium aluminate, containing two metals, is excluded by the limits of the examination, and the question implies that ammonia is added directly to the alkaline liquid.

Sodium silicate is described in books as *soluble in water*, and in a sense it is so; but let A. P. S. buy some, and

tell us how long it takes him to dissolve it. I have recently done so, and have digested it for some weeks in water with only partial solution.

A candidate should hardly be expected to answer questions which do not accord with ordinary laboratory experience.—I am, &c.,

A. X.

December 11, 1886.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 22, November 29, 1886.

Contribution to the History of the Decomposition of Amides by Water and Dilute Acids.—MM. Berthelot and André.—The authors maintain that the decomposition of ammonical salts by water must be taken into account in the analytical study of complex organic matters capable of yielding small quantities of ammonia when distilled with water. The action of acids varies in intensity according to the nature of the amide. It is almost instantaneous with potassium cyanate, slower, but well marked, with urea, and still noteworthy with asparagine and oxamide. The action increases with temperature and concentration. On operating, not with amides derived directly from ammoniacal salts, but with amine-alcohols, the results are of a different nature. The splitting up of complex amides often reproduces, at first amines sparingly, or not at all volatile, which cannot be determined by distillation with magnesia.

Fluorescences of Manganese and Bismuth.—Lecoq de Boisbaudran.—The author describes the fluorescence produced by manganese and bismuth, added to salts of calcium, magnesium, cadmium, strontium, and zinc.

Silver Phosphates and Arseniates.—A. Joly.—The author has examined and described the compounds PO_8Ag_3 , $\text{PO}_8\text{Ag}_2\text{H}$, AsO_8Ag_3 , AsO_8AgH_2 , and AgO, AsO_5 .

Certain Coloured Reactions of the Titanic, Niobic, Tantallic, and Stannic Acids.—Lucien Lévy.—(See p. 300).

New Procedures for Preparing Crystalline Carbonates.—L. Bourgeois.—The author describes the results of two processes in the wet way, both founded on the precipitation of a superheated saline solution by means of ammonium carbonate.

Bulletin de la Société Chimique de Paris.

Vol. xlv., Nos. 5 and 6, September 20, 1886.

Chemico-dynamical Studies on the Reaction of Ferric Salts and of Oxalic Acid under the Influence of Heat.—G. Lemoine.—Ferric chloride and oxalic acid in aqueous solutions are mutually dissolved in the dark under the simple influence of heat. The products are ferrous chloride, hydrochloric acid, and carbonic acid. Ferric sulphate and nitrate undergo a similar decomposition with oxalic acid. The decomposition only begins above 50° , and is accelerated by an increase of temperature. The reaction is also promoted by an addition of water. The author compares the effects of heat to those of light. When the mixture of oxalic acid and of ferric chloride is decomposed in the cold on exposure to the sun, two independent influences come into play: the physical absorption of the active luminous rays and the chemical decomposition of the mixture, this latter taking place according to the same laws as by heat. Various reasons lead him to believe that in the reactions effected by light the

effects observed result simply from the super-position of these two laws.

Distribution of a Base between Two Acids; the particular case of the Alkaline Chromates.—Paul Sabatier.—In such cases Prof. Thomsen considers that the distribution is defined by the relative avidities of the two acids as regards the base, this avidity being a characteristic coefficient of each acid, varying with the base and absolutely independent of the neutralisation heats. On the contrary, M. Berthelot holds that the mechanism of saline reactions may be entirely foreseen according to thermic considerations alone. The author's experiments seem to him decisive in favour of the views of Berthelot.

Reaction of Barium Carbonate and Sodium Sulphate under the Influence of Pressure.—W. Spring.—The author has formerly described results obtained by submitting to intense pressure mixtures of barium sulphate and sodium carbonate, and has found that these two bodies, although both in the solid state, enter into reaction at the ordinary temperature. He has now completed his investigations by the study of the inverse phenomenon, the action of sodium sulphate with barium carbonate. These two substances in fine powder and thoroughly dry were then mixed together and studied under the action of pressure alone, then under that of pressure and time, and lastly under that of pressure and temperature. Pressure alone for a few moments transformed 59.16 per cent of the barium carbonate into barium sulphate. It is to be noted that mere agitation without pressure effected the conversion of 49.79 per cent. In the joint action of pressure and time a limit is reached which marks the end of the reaction. At the temperature of 160° degrees applied for six hours the formation of barium sulphate only reached 34.66 per cent, so that heat interferes with the action of pressure.

Preparation of Calcium Sulphide having a Violet Phosphorescence.—A. Verneuil.—Already noticed.

Researches on Cyclamose.—G. Michaud.—The author has obtained from *Cyclamen europæum* a new sugar of the type $C_{12}H_{22}O_{11}$. Its rotatory power is -11.40 , and after inversion -66.54 .

Urethane from an Analytical Point of View.—G. Jacquemin.—If to a solution containing 0.00005 grm. urethane per c.c. there is added potassa and then mercuric chloride drop by drop, each drop of the latter produces a yellow precipitate, which re-dissolves as long as any urethane is present, and finally the yellow precipitate becomes permanent.

Detection of Urethane in Urine.—G. Jacquemin.—Urethane is extracted by means of ether. Three hundred shakings at least are needed, and after decantation it is repeatedly washed with water. The residue after the evaporation of the ether is taken up in very little water and treated as it has been indicated in the foregoing paper.

Moniteur Scientifique, Quesneville.
3rd Series. Vol. xvi., September, 1886.

Patents taken out in Berlin with Reference to Colouring-Matters.—F. No. 2479. Meister, Lucius, and Bruning. March 17, 1886. Process for preparing metoxyquinoline.

F. No. 2615. No inventor's name. February 13, 1886. Preparation of blue-green colouring-matters, and more especially of the sulphonic acids of the benzylated pseudo-rosanilines.

Sch. No. 3819. Schœlkopp Aniline and Chemical Company, of Buffalo. December 22, 1885. Red and yellow colouring-matters derived from a new naphthol-disulphonic acid.

B. No. 6519. Baden Aniline Company. February 25, 1886. Preparation of solutions of basic aniline colouring-matters, and of colours for printing by means of the

acetines, aceto-chlorhydrines, and chlorhydrines of glycerin.

L. No. 3387. Leipzig Aniline Works. October 21, 1885. Process for preparing blue colouring-matters by the combination of diazo-saffranines with phenols.

H. No. 2728. Alfred Hern, of Bâle. March 17, 1886. Process for preparing chlorides of the dialkylamido-thio-benzoic acids, and of the corresponding acids, as well as of tetra-alkyldiamido-thio-acetones, by means of carbon chlorosulphide and of the tertiary aromatic amines.

P. No. 2732. Pistor, of Bergnenstadt. March 20, 1886. Process for preparing a gall-nut ink. The inventor steepes finely divided metallic iron with a solution of 1 part of pure tannin in 20 parts of water, adding to the product phenic acid, and strengthening the ink by means of suitable colouring-matters. This ink is free from gum, and fast as against air and light.

F. No. 2684. Meister, Lucius, and Bruning. February 1, 1886. Process of preparing compounds of aromatic hydrazines with levulic acid.

MISCELLANEOUS.

Native Alloy of Nickel and Iron.—At the meeting of the Geological Society on December 1st the President announced that he had received from Prof. Ulrich, of Dunedin, N. Z., the announcement of a very interesting discovery which he had recently made. In the interior of the South Island of New Zealand there exists a range of mountains, composed of olivine-enstatite rocks, in places converted into serpentine. The sand of the rivers flowing from these rocks contains metallic particles which, on analysis, prove to be an alloy of nickel and iron in the proportion of two atoms of the former metal to one of the latter. Similar particles have also been detected in the serpentines. This alloy, though new as a native terrestrial product, is identical with the substance of the Octibeha meteorite, which has been called octibehite. Prof. Ulrich has announced his intention of communicating to the Society a paper dealing with the details of this discovery—which is certainly one of the most interesting that has been made since the recognition of the terrestrial origin of the Ovifak irons.

The Mineral Resources of the United States, 1885. United States Geological Survey.—We have received, from the chief of the Division of Mining Statistics, a digest of the principal totals of the various mineral products for 1885. These products are classified into metallic and non-metallic. In the first group we note that the annual decrease in value which was apparent in the three previous years is still noticeable, though not to such a great extent in the year with which this report deals. The falling off from 1884 to 1885 is about 5,000,000 dollars, while that in the previous year was over 16,000,000 dollars; the most remarkable fall of value being that of crude platinum, which in 1882, 1883, and 1884 was worth 3 dollars per ounce, is estimated in 1885 at only 0.75 dollar per ounce. In the non-metallic group the decrease of the previous years has disappeared, and an increase of value—20,000,000 dollars—is apparent, principally in natural gas, coal, and anthracite. In spite of this, however, the grand total is considerably lower than that of 1883, when the figures were over 452,000,000 dollars, those in 1885 being a little more than 428,500,000 dollars.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—London Institution, 5.
Medical, 8.30.

TUESDAY, 21st.—Institution of Civil Engineers 8.
Pathological, 8.30.

THURSDAY, 23rd.—Telegraph Engineers, 8.
London Institution, 6.

THE CHEMICAL NEWS.

VOL. LIV. No. 1413.

CHEMISTRY OF ESTUARY WATER.*

By HUGH ROBERT MILL, D.Sc., F.R.S.E., F.C.S.,
Of the Scottish Marine Station.

OCEAN Chemistry has received much attention since the middle of last century, but the results of older workers have been entirely set aside by those of Forchhammer,† published in 1865, and of Dittmar,‡ on the *Challenger* waters in 1884. It has been fairly established that ocean water—except at very great depths, where there is a slight increase in dissolved calcium carbonate—differs in various positions only in salinity, *i. e.*, the ocean is composed of solutions of different strengths of a saline mixture of uniform quantitative composition.

Very recently much work has been done by the German Scientific Commission in Kiel, and by the German and Norwegian Governments, in examining the physical and chemical characteristics of the water in the North Atlantic, the Baltic, and the North Sea. None of these researches included estuaries, which form in one sense the most interesting field for marine chemical research, on account of the great variety of changes which may be expected alike in salinity and in the composition of the dissolved solids and gases, brought about by the different nature of rivers and the geological features of the districts they drain.

The first essential to be ascertained in examining the chemical conditions of an estuary is the distribution of salinity, or the ratio of total dissolved salts to the water containing them. This can be ascertained in several ways: the most rigidly accurate is to perform a quantitative analysis, and estimate each acid and base; the next which suggests itself is to evaporate a weighed sample of the water to dryness, and weigh the dried residue, making due allowance for the loss of hydrochloric acid from dissociating magnesium chloride, and of carbonic anhydride from acid carbonates. These are too tedious for systematic use when a number of determinations have to be made; and since recent researches have shown that by determining any one constituent of sea water salts the total dissolved matter can be calculated, and that the density of sea water is a function of salinity and temperature, investigators have been accustomed to

measure salinity either by determining the amount of chlorine or the density. The variations from absolute uniformity of composition of the dissolved salts of sea and estuary water do not appear sufficient to invalidate this method for use in river entrances.

The attempt to perform chlorine determinations in a floating laboratory has been discontinued by most chemists, although Tornøe appears to have got good results in this way on the Norwegian expedition. When I commenced work on the chemistry of the Firth of Forth chlorine determinations formed part of the routine observations, but I soon found that, on account of sea spray in the air, it was impossible to make accurate determinations. I consequently employed the hydrometer, and for purposes of general classification used the figures for density reduced to constant temperature (15.56° C. to compare with Buchanan's *Challenger* work) as representing salinity. The hydrometer used was a glass cylinder about a decimetre long, 5 centimetres in diameter, with a loaded bulb below and terminating above in a decimetre-long stem, 3 millimetres in diameter, graduated in millimetres. The instrument was weighed, its volume determined at two temperatures, and the volume of each division of the stem ascertained. In order to adapt it for use in water of any density, small weights of known value could be affixed at the top of the stem. In each case two readings were taken, the first by adjusting the weights so as to read on the lower third of the stem, the second by putting on an additional piece of brass, which sunk it until not more than the upper third remained unsubmerged. From the two readings, and the temperature as taken before and after the observation, the immersed volume and total weight of the hydrometer were obtained, and from these the density was calculated. The mean of the two results was reduced to 15.56° , and taken to represent the salinity of the sample.

Water samples were collected by means of a new form of slip water-bottle,* specially devised for use in shallow water where there are rapid currents, and density was either determined on board the steam-yacht *Medusa*, in the floating laboratory at Granton, or on shore.

The distribution of salinity in the Firth of Forth has been pretty clearly established, and the observations made during the past two and a half years may be briefly enumerated and tabulated.

The River Forth runs east, and at Alloa expands into the estuary, which gradually increases in depth to about 20 fathoms at Inchkeith and 30 near the Isle of May, where the Firth merges into the North Sea close to the mouth of the estuary of the Tay.

Observations of surface, bottom, and intermediate-depth water were made about once a month, at intervals of every 5 miles from Alloa to the Isle of May, a distance of 55 miles, and the stations numbered I. to XII. The figures in Table I. are represented in the curves Fig. 1.

* A Paper read before the British Association, Birmingham Meeting, Section B.

† *Phil. Trans.*, clv., p. 203.

‡ *Chall. Rep. Phys. Chem.*, (1884), vol. i., part 1.

* *Proc. Roy. Soc. Edin.*, January, 1886.

TABLE I.—Density at 15.56° C. (60° F.) of Water in Firth of Forth.

Station.	High Tide.		Low Tide.		All Cases.†					
					Surface.			Bottom.		
	Surf.	Bott.	Surf.	Bott.	Max.	Min.	Mean.	Max.	Min.	Mean.
I.	—	—	—	—	1.00160	0.99923	1.00047	1.00146	0.99939	1.00043
II.	1.01578	1.01891	1.00553	1.00916	1.01981	0.99978	1.01081	1.02020	1.00916	1.01566
III.	1.02073	1.02214	1.01703	1.02056	1.02249	1.01084	1.01888	1.02281	1.01876	1.02124
IV.	1.02235	—	1.02149	1.02385	1.02414	1.01758	1.02192	1.02398	1.02371	1.02385
V.	1.02342	1.02448	1.02303	1.02447	1.02461	1.01863	1.02323	1.02509	1.02366	1.02448
VI.	1.02406	1.02562	1.02357	1.02486	1.02496	1.01953	1.02383	1.02562	1.02484	1.02505
VII.	1.02485	1.02497	1.02471	1.02494	1.02528	1.02380	1.02477	1.02533	1.02419	1.02496
VIII.	1.02502	1.02531	1.02501	1.02538	1.02555	1.02450	1.02501	1.02562	1.02514	1.02535
IX.	1.02515	1.02533	1.02512	—	1.02553	1.02465	1.02513	1.02541	1.02526	1.02533
X.	1.02522	1.02554	1.02530	1.02508	1.02563	1.02470	1.02526	1.02554	1.02508	1.02531
XI.	1.02542	—	1.02521	1.02530	1.02566	1.02417	1.02532	1.02571	1.02424	1.02530
XII.	1.02552	1.02549	1.02534	1.02554	1.02570	1.02443	1.02546	1.02562	1.02460	1.02551

At Inchkeith there is practically no tidal range of salinity, but further up the estuary there is considerable difference between salinity at high and low tide; the shoaling of the river above Queensferry does not appear to affect the increasing divergence of the curves (see fig. 1). The great uniformity and close approximation of surface and bottom salinity in the outer half of the Firth is extremely interesting, for it shows the river diffused in a homogeneous manner through a wall of salt water, which is never the case in a stream running directly into the sea. Beyond the Isle of May there is a dip in the line of surface density not followed by that for the bottom. This I have shown to be due to the influence of the River Tay.*

As a whole the Firth seems to be in a state of equilibrium as regards salinity; the fresh water entering it must pass through it at a definite rate, and bear a constant ratio to the sea-water at each point. It is a matter of much interest to find this ratio, and thence to deduce the actual amount of each kind of water in the Firth.

When river- and sea-water mix a slight contraction takes place, but this may be disregarded at the present stage of the enquiry; and by assuming that fresh and salt water mix without change of volume, and taking 1.000 as the density of river water and 1.026 as that of sea water, the percentage of each at different parts of the Firth has been calculated, and is shown in Table II. The Table also shows the number of square yards of cross section occupied by each kind of water—supposing the river water to be separated from the sea water—at each station 5 miles apart.

TABLE II.

Station.	High Tide.		Low Tide.		Mean of all Tides.	
	Per cent.		Per cent.		Square yds. in cross section.	
	Fresh water.	Sea water.	Fresh water.	Sea water.	Fresh water.	Sea water.
I.	95.5	4.5	100.0	0.0	776	37
II.	38.2	61.8	76.8	23.2	1,358	1,532
III.	19.8	80.2	33.7	66.3	2,440	8,660
IV.	13.5	86.5	16.8	83.2	3,900	26,100
V.	9.7	90.3	11.2	88.8	4,040	47,960
VI.	7.1	92.9	9.0	91.0	7,360	107,640
VII.	4.5	95.5	—	—	12,100	289,900
VIII.	3.7	96.3	—	—	16,700	579,300
IX.	3.5	96.5	—	—	17,100	626,900
X.	2.6	97.4	—	—	16,800	630,200
XI.	2.6	97.4	—	—	25,300	945,700
XII.	1.9	98.1	—	—	30,300	1,562,700

The Firth of Forth contains 824×10^6 tons of river water; and at low tide $28,000 \times 10^6$ tons of sea water, with 4000×10^6 tons of sea water additional when the tide is high. The total volume of the Firth at low water is $36,700 \times 10^6$ cubic yards, according to the soundings of the Admiralty charts. The discharge of river water is about 11,000 cubic yards a minute at Alloa, so that, if no other supply were available, two years' accumulation of river

water exists in the Firth of Forth. The freshening influence of rain is probably too small to affect this value much; the various tributary rivers must modify it to some extent, but their action cannot be allowed for as their discharge is unknown.

The figures in Table II. show an actual increase in the amount of fresh water diluting the sea water in each successive section of the Firth, and this increase—analogueous to that observed by Birch in the Thames—is too great to be wholly accounted for by the contributions of tributaries. It is evident to my mind that in the outer part of the Firth of Forth diffusion is the great agent in carrying river water seaward; and as the diffusion takes place across sections where the difference in salinity of the substances diffusing into each other becomes less and less, the rate must become slower and slower. An accumulation of river water in the seaward reaches would thus be accounted for, since in each very thin slice the difference of salinity on the side by which the fresher water enters is greater than that on the side by which it leaves, and *cæteris paribus* the rate of diffusion is proportional to difference in salinity.

The Clyde water system differs completely from that of the Forth, and a different distribution of salinity has been found there. Table III. shows the density of water in the Firth of Clyde and in the Clyde sea-lochs, in April and June this year. It may be viewed as an extension of Macadam's paper read to this Section in 1855.* Each of the regions for which the density is given was sounded in four or five places, samples of water taken at surface, bottom, and intermediate depths, and the mean of all the samples taken for each position put down on the Table. The Firth of Clyde is barred by a plateau rising to within 25 fathoms of the surface at its communication with the sea; inside it is the deep Arran basin of over 80 fathoms, and indirect communication, so far as surface water is concerned, the separate basin of Upper Loch Fyne. Loch Strivan is a similar smaller basin, communicating with the Kyles of Bute on one side, and with the plateau between the Arran and Dunoon Basins on another. The Dunoon Basin bears the same relation to Loch Long and Loch Goil than the Arran Basin does to Loch Fyne, but it is further up the estuary. The Holy Loch is a shallow bay, and the Gare Loch a shallow basin connected with the upper part of the estuary. The sea-lochs, as a rule, preserve at the bottom water of the salinity that prevails in the Firth at their mouth; while in several cases, notably in that of Loch Long, the surface water is greatly diluted by streams and temporary torrents.

The whole mass of water was fresher in April than in June, a result comparable with the state of matters in the Baltic, as determined by the Kiel Commission, and probably due to a similar reason, the melting of snow. The curve of salinity from river to sea along the estuary and firth of Clyde appears to resemble that for the Forth; but it has not yet been sufficiently worked up to enable one to form an exact judgment. The curves for the Tay and

* Proc. Roy. Soc. Edin., xiii. (1885), p. 347.

* Brit. Assoc. Rep., (1885) ii., 64.

TABLE III.

Place.	April, 1886.		June, 1886.		Mean of April and June.	
	Surf.	Bott.	Surf.	Bott.	Surf.	Bott.
Irish Channel	1.02535	1.02532	1.02533	1.02534	1.02528	1.02533
Clyde Plateau	1.02398	1.02504	1.02479	1.02528	1.02438	1.02516
Arran Basin	1.02256	1.02509	1.02460	1.02504	1.02358	1.02507
Loch Fyne.. ..	1.02417	1.02471	1.02439	1.02480	1.02428	1.02476
Loch Strivan	1.02346	1.02483	1.02458	1.02490	1.02402	1.02485
Kyles and Loch Ridush ..	1.02317	1.02401	1.02438	1.02484	1.02378	1.02442
Dunoon Basin	1.02037	1.02469	1.02369	1.02487	1.02203	1.02478
Holy Loch.. ..	1.01438	1.02415	1.02228	1.02426	1.01833	1.02420
Loch Long	1.01557	1.02439	1.01661	1.02442	1.01609	1.02440
Loch Goil	1.02036	1.02449	1.02384	1.02452	1.02210	1.02450
Gareloch	1.02052	1.02345	1.02329	1.02340	1.02190	1.02343

Thames* resemble each other in being more gradual than that for the Forth, and in the two former river systems estuarine conditions are carried further out to sea than in the last named.

In order to detect any deviation from uniformity between the composition of estuarine and ocean salts, the best plan is to select some one constituent and determine its ratio to the total dissolved matter, or, which amounts to the same thing, to the density as determined very accurately at some constant temperature, say by means of Sprengel tubes at 0° C. It was because my chlorine results were not sufficiently precise for treatment in this way that I gave up observing that quantity while investigating salinity; but the observations I made appear to indicate a difference in the ratio for estuary water, a result which was certainly found by Gibson in the Moray Firth.†

sorting process by diffusion. My observations as yet do not show whether this is the case or not, but a series of analyses of water taken at certain selected places is about to be commenced in order to decide for or against the theory.

As river-water salts differ from those of sea-water chiefly on account of the amount of silica and calcium carbonate they contain, it is of great interest to trace the proportion of these in different parts of estuaries. The abundance of silica is proved by the enormous development of diatoms in estuaries as compared with those in salt seas, but I have not yet made any exact experiments on the matter. The question of carbonates in sea water has given rise to a great deal of controversy, in which I do not desire, for the present, to join. Tornøe's method of alkalinity determination, as improved by Dittmar,

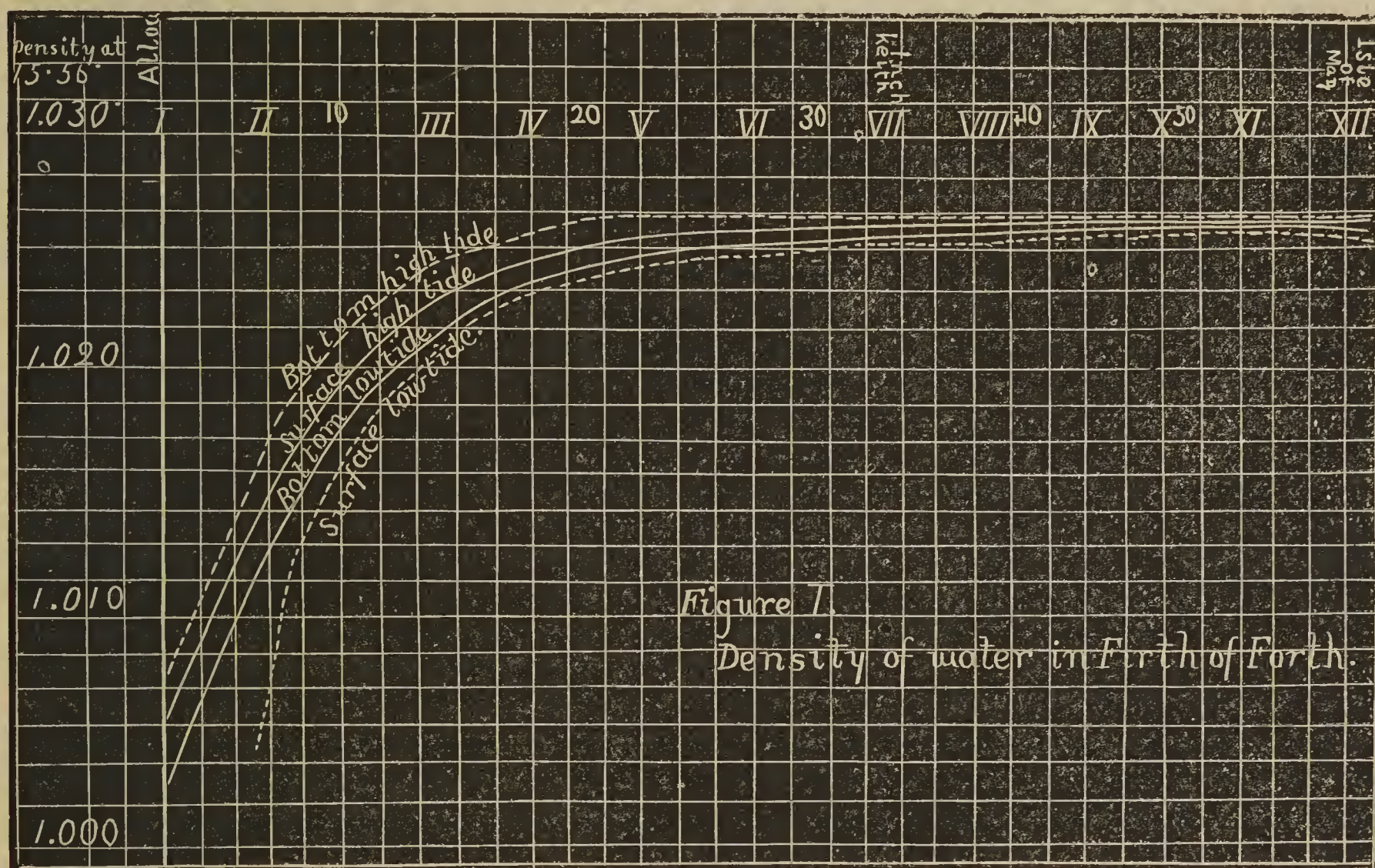


Figure 1.
Density of water in Firth of Forth.

Water from the river Forth, above Stirling, contains, according to a number of determinations of the total solids, 5.8 grains per gallon, or 7.89 parts per 100,000; and 8 per cent of silica was found in this solid matter. The water contains 1.9 grains of chlorine per gallon, or 2.7 parts per 100,000, which corresponds to 34 per cent of the total salts. This is a much lower ratio than that (55.4 per cent) found in sea-water; but the disturbance of the chlorine ratio of the water in the Firth, due to this cause, must be entirely imperceptible.

It is not certain, however, that the river-water salts do not affect the chlorine ratio; for, although there is 5 per cent of river water in the Firth at Inchkeith, to take an example, it does not necessarily follow that just 5 per cent of the quantity of each component of the dissolved solids of river water are present. If river water mixes with the sea by diffusion, one salt may diffuse more rapidly than another, and there may be an accumulation of particular salts at particular places. In fact, the presence of fresh water in the Firth not only introduces fresh-water salts, but, by producing a constant gradient of density, it gives opportunity to the constituents of sea-salt to undergo a

seems the best adapted for obtaining a general knowledge of the variation in amount of dissolved calcium carbonate from place to place, for there can be no doubt that the alkaline reaction shown by sea water is due to dissolved carbonates, and the chief of these, it is safe to assume, is that of calcium. The method consists of measuring 250 c.c. of the filtered water into a porcelain basin, running in a quantity of standard hydrochloric acid, made up to such a strength that 1 c.c. contains acid equivalent to 1 m.g. of normal calcium carbonate (CaCO_3), boiling for twenty minutes to expel carbonic anhydride, adding a few drops of aurine indicator, and titrating the excess of acid by means of standard alkali solution of equivalent strength.

In order to render them comparable all observations of alkalinity were reduced to their value for the standard sea-water (density 1.026) they contained, and alkalinity was measured in the number of c.c. of standard acid required per litre, i.e., the number of m.g. of calcium carbonate per litre. In this way, if the observed alkalinity of a sample with density 1.01265 were 26 m.g. per litre, this quantity was multiplied by 2, and the alkalinity of the true sea-water, which formed half its volume, taken as 52 m.g.

Table IV. gives the mean alkalinity observed in the estuary and Firth of Forth from Station III. to Station X.

* From Birch's chlorine results, *Min. Proc. Inst. C.E.*, lxxviii., 212, and lxxx., 295.

† "Fishery Board for Scotland, 4th Annual Report, 1885."

Table IV.

Station.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Surface..	56.1	56.2	56.2	54.5	52.9	52.7	52.9	52.8
Bottom..	54.1	—	53.0	—	52.7	—	—	—

Speaking generally we can say that alkalinity increases when density decreases, or when the river-water relatively rich in carbonates increases in amount.

Near the river Spey, which has no estuary, alkalinity was found to increase as soon as the brackish water surrounding the river mouth was entered from the sea.

The most difficult, and perhaps the most important, part of chemical research on estuaries has not yet, to my knowledge, been commenced. It is the investigation of dissolved gases, their nature and amount, as influenced by salinity. For this it is necessary to know the salinity in the first place, and its variation from point to point. This preliminary work is what I have been principally engaged in.

NEW PROCESS FOR THE VOLUMETRIC DETERMINATION OF ZINC IN POWDER.

By F. WEIL.

THE author's processes for the volumetric determination of copper by means of hydrochloric acid in very large excess, and of stannous chloride, which he has already applied to the speedy and exact titration of antimony, iron, sulphur in sulphides, sugar, and glucose, have led him to a quick and accurate method for titrating the metallic zinc in zinc-powder and granulated zinc.

He prepares a copper solution such that 10 c.c. may contain exactly 0.1 gm. of pure copper. For this purpose he dries, in a porcelain capsule, pure copper nitrate, the final ignition of which is completed in a platinum crucible over a Bunsen. The pure copper oxide thus obtained is let cool in a desiccator, and 12.519 grms. are weighed out and dissolved in a slight excess of pure hydrochloric acid with the aid of heat. The liquid is then made up with distilled water to the exact volume of 1 litre. It is stirred up, and thus yields a normal solution, 10 c.c. of which contain exactly 0.1 gm. of pure metallic copper.

By means of a pipette 50 c.c. of this liquid are placed in a porcelain capsule, and neutralised with ammonia until a slight turbidity appears, which does not disappear on stirring. At this moment the liquid should still be faintly acid. The portion weighed out for analysis (0.4 gm. of the zinc powder) is let fall to the bottom of the capsule, and this little heap is covered with a platinum wire, which is coiled up at its lower end into a flat spiral, whilst the stem stands up out of the bath to serve as a handle for stirring occasionally.

The zinc precipitates copper equivalent for equivalent. The operation at the ordinary temperature may be completed in ten minutes if a platinum capsule is used. The end of the reaction is indicated exactly by a platinum wire with which the powder at the bottom of the liquid is touched. If any zinc remains undissolved the wire becomes coated with a slight black or red layer. If, on the contrary, the platinum indicator remains of a bright white, all the zinc is dissolved and the operation is at an end. The platinum wire is then withdrawn, washed with the washing bottle, and acetic acid is poured into the capsule, drop by drop, to render limpid the liquid at the bottom of which is the reduced copper. The supernatant solution is decanted into a vessel graduated at 100 or at 200 c.c. The capsule and the copper are sufficiently washed with distilled water; the washings are added to the bulk of the liquid, which is then made up to 100 or 200 c.c. It is stirred, let settle, if needful for some minutes; 10 c.c. of the clear liquid are put into a small flask of white glass. From two to three times its volume

of pure hydrochloric acid are added, and the liquid is titrated at a boil until completely decolourised with a solution of stannous chloride which has been standardised with a dilute solution of copper containing 0.04 gm. of pure copper in 10 c.c. The result shows the quantity of copper in excess remaining in the solution. On deducting it from the 0.5 gm. of copper used we obtain the weight of copper precipitated by the sample of zinc. On multiplying it by the coefficient 1.0236—

$$\left(\frac{Zn=32.5}{Cu=31.75} = 1.0236 \right),$$

we find the quantity of metallic zinc contained in the 0.4 gm. of zinc powder operated upon.—*Comptes Rendus*, vol. ciii., p. 1013.

NOTE ON THE ANALYSIS OF HOOFS AND HORNS.

By JOHN HUGHES, F.C.S., F.I.C.

FINELY ground hoofs and horns, sometimes called keronikon, are now used by manure manufacturers as an economical material for supplying organic nitrogen in a concentrated form.

It contains from 14 to 15.35 per cent of nitrogen, and though naturally hard and tough, yet when ground and treated with acid it soon becomes resolved into available plant-food.

As sampled on delivery at the works, it is in the condition of a granulated meal, of a brown colour, and sufficiently fine that the greater part will pass through a sieve having holes $\frac{1}{8}$ inch diameter.

This is rather too coarse for the analysis, especially as the mineral impurities consist of dirt, sand, small stones, and particles of iron, which requires that a fair portion should be ground up into a fine powder previous to weighing 0.7 and 0.6 gm. respectively for duplicate nitrogen determinations.

Now during the process of grinding in an iron mortar the material becomes more hygroscopic, and as it is reduced to a fine powder absorbs moisture in proportion to the increased surface presented to the atmosphere, this property being specially marked during damp weather, such as at presents obtains, and in the case of samples which are richest in nitrogen and have least foreign impurity.

It follows, therefore, that the fine portion analysed contains less nitrogen than the original coarse sample received, and it is necessary to make a proportional correction in the form of a slight addition in order to obtain the correct results for the certificate.

To what extent this increase of moisture applies will be seen from the following particulars in three samples:—

I. In fine portion analysed—

	A.	B.	C.
Water dried at 212° F...	5.03	6.52	6.30
Mineral matters	4.50	4.85	7.52
Organic matters	90.47	88.63	86.18
Containing nitrogen ..	14.80	14.53	13.96

II. In coarse sample received—

Water dried at 212° F...	3.14	5.73	5.33
Nitrogen (calculated) ..	15.09	14.65	14.11
Equal to ammonia ..	18.32	17.78	17.13

The quantities of the coarse and fine taken for the water determinations were in each case the same, as well as the length of time allowed for drying.

The portions from B sample were spread out on paper over night and re-weighed the next morning, when it was found that not only was the water previously driven out

by drying re-absorbed, but there was a substantial increase, the fine portion containing 8.12 and the coarse portion 6.32 of water.

In the case of another sample, the fine portion, which had lost 4.66 by drying, was allowed to remain over night in the platinum basin just as taken from the balance and without being in any way disturbed or spread out, and when re-weighed was found to contain 6.49 per cent, having, in fact, absorbed an additional 1.83 per cent of water—the temperature of the room being about 50° F. and the weather damp.

It is evident, therefore, that fine grinding materially increases the hygroscopic properties of such hoofs and horns; and although the correction in the nitrogen due to the absorbed water is really not usually very large, it nevertheless should be made. This is the more necessary as many commercial contracts require that when the ammonia results of the two selected chemists differ more than 0.50 per cent, another sample is to be sent to a third chemist.

In a "Note on the Analysis of Shoddy," published in the CHEM. NEWS (vol. xlii., p. 325), 1880, the writer pointed out that the chief cause of the frequent and great differences in the ammonia results which then existed was chiefly caused by the omission of some chemists to make the necessary correction for the moisture lost during the preparation of the sample. The consequence being that the results were reported much too high, especially in those cases where the official samples were at all damp. In fact, the ammonia was given as found in the partially-dried portion analysed instead of for the original damp sample received.

In the analysis of ground hoofs and horns, however, it is probable that the results sent off are not unfrequently rather too low, especially as these highly nitrogenous materials require special care and attention in order to get the whole of the nitrogen compounds converted into ammonia during the process of combustion.

Having had some experience in testing these samples, it may be of use to mention that it is desirable to be liberal in the quantity of soda-lime; at least 20 grms. should be mixed with the 0.7 gm., and a couple of inches of it should be in front of the nitrogen mixture; while the time allowed for burning should be not less than 1½ to 2 hours.

Finally, from the fact that of the two determinations always made, the one in which 0.6 gm. was mixed usually gave the higher result as compared with 0.7 gm. and similar quantities of soda-lime, it is believed that the whole of the nitrogen is scarcely ever completely recovered as ammonia, and that, consequently, the higher results when obtained should be regarded as the more correct.

Analytical Laboratory, 79, Mark Lane, E.C.,
Dec. 13th, 1886.

REICHERT'S METHOD OF BUTTER ANALYSIS.*

By H. B. CORNWALL and SHIPPEN WALLACE.

THE authors recommend that Reichert's process be performed as directed by himself (*Zeits. f. Anal. Chem.*, 1879, p. 68), because it is a strictly comparative one, not to be arbitrarily altered. Their experiments with an inverted condenser show that there is no appreciable loss by escape of butyric ether. It is important to make a blank test with the alcohol and potash employed. The authors did this, and also deducted the amount of decinormal alkali solution thus consumed from the results of their tests on butters.

* Abstracted from the Ninth Report of the State Board of Health of New Jersey, U.S.A., by H. B. Cornwall.

The especial object of the paper was to test the correctness of Reichert's conclusions as to the average and minimum standards for butter, and also Munier's proposal to greatly lower Reichert's standard for certain seasons of the year (*Zeitschrift*, 1882, p. 394). Munier's proposed standard was 10 c.c. of decinormal alkali (for 2.5 grms. of pure butter fat) from October to March; 12.1 c.c. from March to May; 12.4 c.c. from May to August; and 11 c.c. from August to October.

The average quantity of decinormal alkali consumed by the authors was 13.68 c.c. They tested eighty pure butters, made in three widely different parts of the State, for this purpose, and each butter from the milk of a single cow. The results indicated that there was no apparent connection between the c.c. of decinormal alkali consumed and any of the following conditions: season of the year; breed, food, or age of the cows; or time after calving. The average in the case of one series of tests was actually higher for November and December than for September and October.

The authors are unwilling to accept Munier's results until further confirmed, for the following reasons:—First, he appears to put little confidence in his own results, because he found one butter (in December) consuming only 9.2 c.c. of decinormal alkali, and yet he does not propose a lower standard than 10 c.c. even for December. Second, his figures are, for the most part, very low as compared with all other observers, his average for sixty-nine butters being only 12.07 c.c., against an average of 13.89 for 162 butters reported by eight or ten other experimenters, including the authors, some of the experimenters having purposely selected Dutch breeds of cows. Notwithstanding that Munier's results have been attacked by several writers, the authors have not seen any reply to the criticisms, nor any defence of the figures obtained by him from butters furnished by the "Israelitische Molkerei" and other Amsterdam creameries.

The authors recognise the fact that the proportion of volatile (soluble) fatty acids obtainable from different pure butters may vary much, and therefore strongly recommend that tests made with a view to establishing minimum and maximum standards for the fatty acids (whether soluble or insoluble) should be made on butters known to be the product of single cows, such butters often being offered for sale.

The authors find it necessary to recommend that the standard for butter (unless surely known to be made from the mixed milk of several cows) should be made lower than the 12.5 c.c. proposed by Reichert, or even the lower limit of 11.5 to 12 c.c. proposed by Sendtner (*Wagner's Jahresbericht*, 1883, p. 979). One cow was found to yield butter requiring only from 11.3 to 11.5 c.c. of decinormal alkali (after deduction of 0.3 c.c. for the decinormal alkali consumed in a blank test, as already described). Butter was made from the milk of this cow in the beginning and at the end of December, and it was tested by both of the authors, each working in his own laboratory and with entirely different sets of reagents. They obtained identical results, and therefore believe that, for butter from the milk of a single cow, the minimum standard cannot safely be above 11 c.c. of decinormal alkali consumed in Reichert's test, when 2.5 grms. of fat are taken.

The cow yielding this butter was one of a herd of eight cows in Princeton, New Jersey. She was of mixed breed, chiefly Alderney; was nearly five years old; had a calf eight months before, and was expected to have another in the following May; she yielded at the time from six to seven quarts (roughly estimated) of good milk daily; was fed on barley meal and corn-stalks (maize), and appeared to be in good condition. The butter, made separately from five other cows in the same herd, at nearly the same time, used from 12.2 to 15.1 c.c. of decinormal alkali, so that neither the season of the year nor the food appears to have had any influence on the result.

In case of butter made on the large scale, from the mixed milk of several cows, the standard above proposed

(11 c.c.) is practically equal to the usual one of 12 c.c., because such butter cannot be profitably adulterated without falling much below either standard when tested by Reichert's process.

The authors are very strongly in favour of Reichert's process, both because it is the most rational of the common quantitative methods for testing butter (being founded on the true difference between genuine and imitation butter, which is the amount of readily volatile fatty acids in the two), and because it is as thoroughly a quantitative method as any other, so far as regards the conclusions to be deduced from it. A chemist can announce beforehand (within certain reasonable limits) how much decinormal alkali will be consumed in the Reichert test on a mixture of pure butter fat and a foreign fat (lard, for instance) mixed in known proportions. Can any one do more by any method? Before a Court of Law he can affirm positively that a certain fat is not pure butter, because pure butter always consumes at least so much (say 11 c.c.) of decinormal alkali when tested by Reichert's method. What more definite answer can be required? Aside from its accuracy, the greater facility of Reichert's method should secure its adoption in these days, when so many food analyses are made.

But more than this can be said: one of the authors met with an imitation butter which by Hehner's method yielded only 88.2 per cent of insoluble fatty acids. This butter would have passed as pure by that test, but the Reichert process showed it to be impure (as it really was, being an imitation made from lard and butter, and known as "sueine"), because it only consumed 4.2 c.c. of decinormal alkali.*

ON THE MICRO-CHEMICAL ANALYSIS OF MINERALS.

By T. H. BEHRENS.

(Concluded from page 302.)

THE preceding pages contain the results of a research which I undertook in order to satisfy in some measure the wants and necessities of petrographers. In the course of my work my notice has been attracted by other reactions which would serve to indicate the presence of the rarer elements. I propose communicating them at some future time, provided no other person has got ahead of me in this field. The method I propose, and which is based on the transformation of silicates into sulphates, has so great an analogy to the methods ordinarily in use in qualitative analysis that it is highly probable that we shall be able to apply the test to a much greater number of elements: the certainty of the results obtained, the rapidity of carrying out the reactions, and the modest dimensions of the apparatus required, might have induced me to persist for a longer time in researches of this nature, if I had not been convinced that I ought to use all my available time in studying the second part of this question, the most difficult part of my work, that which aims at finding reactions which will indicate the presence of several chemical compounds on the polished surface of a mineral.

For this reason I have decided to publish the results obtained up to the present, results which leave nothing to be desired in the way of certainty.

I have not hesitated to introduce some of the more important reactions into the practical work of the students at the Ecole Polytechnique, such as the test for potassium,

* A similar proof of the accuracy of Reichert's method has been met with in the writer's experience. A butter was tested by Hehner's method, by a New York chemist of great experience in such work. He reported the butter as of doubtful purity. Tested by Reichert's method subsequently, it consumed 9.2 c.c. of decinormal alkali, and the writer unhesitatingly pronounced it impure. It was finally acknowledged to be so by the dealer. It was one of the so-called "gilt-edge" imitations, which are perhaps not as often detected as they should be.—H. B. C.

calcium, magnesium, and aluminium. This succeeded completely. I can therefore, in full confidence, recommend young microscopists to avail themselves of the methods I have described in the foregoing pages.

If this application of these methods is followed up, it will without doubt lead to the discovery of new and improved ones; I feel convinced that they will be well received by petrographers and microscopists. I for myself shall be only too pleased at every success which may be achieved in this class of research.

To enable the degree of accuracy which can be obtained to be properly judged, and also to make the manner of proceeding as clear as possible, I shall now, in the form of an Appendix, give the details and the results arrived at of several analyses made by me with weighed samples of minerals.

22. Control Analyses.

(1.) 0.2 m.grm. of black tourmaline was heated with hydrofluoric acid. The action was very weak. After heating the powdered mineral very strongly, I succeeded in dissolving about half of it. The dried mass was warmed with sulphuric acid until the action was nearly finished; the residue was boiled with water; and finally the solution, which was about 0.015 c.c. in volume, was taken up by means of a capillary pipette.

Half the solution, evaporated on a plate of glass, gave very distinct crystals of gypsum, and with chloride of caesium such a plentiful supply of caesium alum was formed that one-fifth part of the liquid would have been sufficient to observe the reaction. The other half, saturated with ammonia, gave, after adding a small quantity of phosphorus salt, in the space of about two minutes, a large number of hemimorphic crystals of ammonio-magnesian phosphate.

It will be seen that I did not use more than 0.05 m.grm. of tourmaline for each test, taking the inevitable loss into account. If we admit that this mineral contains 3.3 per cent of alumina, 1 per cent of lime, and 3.3 per cent of magnesia, we get the following results:—

Abundant reaction with	0.017 m.grms. of	Al ₂ O ₃ ,
Sufficient	0.0017	„ MgO,
And	0.0005	„ CaO.

(2.) 0.2 m.grm. of sodalite was decomposed by sulphuric acid; the residue, after evaporation, was boiled with water, and the solution—taken up with a capillary pipette—was divided into two equal parts. One of these halves gave good crystals of gypsum, and with chloride of caesium a few but very distinct crystals of alum were formed.

The second portion, treated with perchloride of platinum, gave numerous octahedra of potassic chloroplatinate. This result, although rather surprising, was confirmed by another trial, using hydrofluoboric and hydrofluosilicic acids as reagents. The formation of the corresponding sodic salts took a considerable time,—in fact the liquid was almost entirely evaporated; the reaction was not so distinct as I could have wished. A tenth of a m.grm. of sodalite corresponds to—

0.03 m.grm. of	Al ₂ O ₃ ,
0.001	„ CaO,
0.0006	„ MgO,
0.0023	„ Na ₂ O.

(3.) 0.1 m.grm. of sodalite was distilled with sulphuric acid in a crucible with a platinum cover. The distillate and the residue, dissolved in water, both gave distinct indications of the presence of chlorine by the reaction with chloride of thallium. If we admit that half the chlorine would go into the distillate, we arrive at the result that we can detect 0.035 m.grm. of chlorine, which corresponds to 0.006 m.grm. of NaCl and 0.05 m.grm. of sodalite.

(4.) 0.2 m.grm. of apophyllite from Andreasburg, warmed with hydrofluoric and sulphuric acids in a crucible with the platinum cover, gave a distillate which deposited

an abundant quantity of fluosilicate of soda, on the addition of sodic chloride. The residue in the crucible was evaporated to dryness, warmed again with a little dilute sulphuric acid, until the sulphuric vapours commenced to be given off, then dissolved in water. Half the liquid, when treated with chloride of cæsium, gave a small quantity of alum and abundant crystals of gypsum. Ammonio-sodic phosphate and ammonia gave no reaction whatever. The other half, treated with perchloride of platinum, produced an abundant crystallisation of potassic chloroplatinate.

I did not succeed in detecting the presence of sodium either with cerous sulphate or with hydrofluosilicic acid.

0.2 m.grm. of apophyllite corresponds to 0.1 m.grm. of silicic acid, half of which would have been detected with the greatest ease; 0.1 m.grm. of apophyllite contains 0.026 m.grm. of CaO and 0.005 m.grm. of K₂O.

As for aluminium, this metal is only mentioned once (1.5 per cent) by Rammelsberg,* as a component part of apophyllite; thus the reaction with cæsic chloride was successfully carried out with 0.0015 m.grm. of alumina.

As hydrofluoric acid might contain traces of alumina, the experiment was repeated with 0.3 m.grm. of apophyllite and concentrated sulphuric acid without the addition of hydrofluoric acid.

The distillate gave, with sodic chloride, a slight crystallisation of sodic fluosilicate, a certain proof of the presence of fluorine. The residue gave abundant crystals of cæsium alum on the addition of cæsic chloride.

If we take the percentage of fluorine in apophyllite, which according to different writers varies from 0.46 to 1.71 per cent (according to Rammelsberg† apophyllite from Andreasburg contains 1.18 per cent of fluorine), as 1 per cent, we find the limit of sensitiveness of the reaction to be 0.003 m.grm. of fluorine.

(5.) 0.4 m.grm. of boracite was distilled with sulphuric acid; the distillate gave, with thallous sulphate, an intense reaction, indicating the presence of chlorine. After having added hydrofluoric acid to the residue, it was re-distilled at a moderate temperature. The volatile product obtained only gave traces of fluoborate with potassic chloride; the same result was found with a product obtained at a more elevated temperature.

In a third experiment the temperature was raised until greyish vapours commence to be given off; the distillate obtained, when treated with potassic chloride, gave, after about five minutes, abundant rhombs and elongated hexagons. The residue was dissolved in water. A fourth part of the liquid, when treated with ammonia and phosphorus salt, gave abundant crystals of ammonio-magnesian phosphate.

0.4 m.grm. of boracite	=	0.034 m.grm. of chlorine.
0.4 " "	=	0.25 " boric acid.
0.1 " "	=	0.031 " magnesia.

(6.) 0.2 m.grm. of axinite was gently warmed with sulphuric and hydrofluoric acids; the volatile product, when treated with sodic chloride, gave abundant crystals of sodic fluosilicate. The residue was again distilled with hydrofluoric acid at a higher temperature, and the vapours were condensed in dilute sulphuric acid.

This distillate, warmed with a drop of hydrofluoric acid until it commenced to take a brown colour (caused by the decomposition of the organic matter coming from the gutta-percha), was mixed with a little water, placed on a plate of varnished glass, and treated with potassic chloride. After the lapse of three minutes I obtained rhombs of potassic fluoborate and some few octahedra of the corresponding fluosilicate.

The residue left in the crucible was treated with boiling water. A third part of this liquid, when treated with chloride of cæsium, gave crystals of cæsium alum; another third gave the same after the reduction of the iron by a few grains of zinc. In the last portion I detected a large

quantity of magnesium by means of the reagents. In all these experiments large quantities of crystals of gypsum were found.

0.2 m.grm. of axinite	=	0.1 m.grm. of SiO ₂ .
0.2 " "	=	0.008 " BO ₃ .
0.07 " "	=	0.012 " Al ₂ O ₃ .
0.07 " "	=	0.0014 " MgO.
0.07 " "	=	0.013 " CaO.

The first and last were very abundant.

(7.) With 0.2 m.grm. of datholite, treated in the same manner, I obtained sufficient indications of the presence of boron, and an abundant quantity of fluosilicate, indicating the presence of silicon.

In the residue were found quantities of crystals of gypsum, but no results were obtained with cæsic chloride or with the salt of phosphorus and ammonia.

0.2 m.grm. of datholite	=	0.076 m.grm. SiO ₂ .
0.2 " "	=	0.04 " BO ₃ .
0.2 " "	=	0.084 " CaO.

(8.) 0.5 m.grm. of pyknite from Altenberg was melted with double its volume of soda; about half was dissolved in concentrated acetic acid. The liquid was evaporated to dryness with sulphuric acid, which is easily done without loss. The product of the distillation, treated with sodic chloride, gave abundant crystals of sodic fluosilicate—a sure sign of the presence of fluorine. 0.2 m.grm. of pyknite contains 0.037 m.grm. of fluorine.

(9.) Felspar from the grey porphyry from Elfdalen, in Sweden, was treated with ammoniac fluoride and hydrochloric acid; the mass was then evaporated with sulphuric acid. A large quantity of gypsum was obtained. Perchloride of platinum indicated the presence of a considerable quantity of potassium; cerous sulphate showed the presence of the two alkaline metals, the sodic salt being much more plentiful than that of potassium.

(10.) The examination of a felspar contained in a rock found at Mängenbach, and which has been called Labrador porphyry, proved that the mineral contained a little calcium, more potassium than the preceding mineral, and a preponderating quantity of sodium.

(11.) Felspar taken from the corsite of St. Lucia, in Corsica. The felspathic needles from the nodules have the same composition as the imperfectly formed crystalline grains, from the stony mass which surrounds the nodules. These two species are very rich in calcium; however, they are not pure calcic felspars; in fact, they contain appreciable quantities of potash and soda.

(12.) Bisilicate of the corsite from St. Lucia. The black powder first takes a greenish tint when attacked with hydrofluoric acid; it then becomes pale and dissolves. This behaviour makes us suspect that the mineral contains some felspathic matter. The examination shows that it contains, besides a large quantity of calcium and magnesium (which confirms the supposition that the mineral is hypersthene), a considerable quantity of potassium and aluminium, and what is very important, these results were obtained with those apparently homogeneous pieces taken from different samples.

Nitrogenous Principles of Vegetable Mould.—MM. Berthelot and André.—The vegetable mould contains a notable proportion of nitrogen. This proportion generally reaches one or two thousandths. Nitrogen exists chiefly in the soil in the form of quaternary organic compounds, almost totally insoluble. The authors find that these little-known principles are amidic bodies, which behave like albumenoid principles, and which generate under the influence of acids, alkalies, and even pure water, a certain proportion of ammonia, and a larger proportion of soluble amidic compounds. The ammonia furnished by the soil experimented on by the authors results almost entirely from certain splittings up effected under the influence of hydrochloric acid at the expense of the insoluble amidic compounds.—*Comptes Rendus*,

* "Mineralchemie," 1860, p. 506.
† *Ibid.*, p. 505.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING NOVEMBER 30TH, 1886.

By WILLIAM CROOKES, F.R.S.,

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford.

and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London
Hospital; Medical Officer of Health for Islington.

To COLONEL SIR FRANCIS BOLTON, *Water Examiner,*
Metropolis Water Act, 1871.

London, December 4th, 1886.

SIR,—We submit herewith the results of our analyses
of the 182 samples of water collected by us during the past
month, at the several places and on the several days indi-
cated, from the mains of the seven London Water Com-
panies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of
samples, one taken daily, from November 1st to November
30th inclusive. The purity of the water, in respect to
organic matter, has been determined by the Oxygen and
Combustion processes; and the results of our analyses by
these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several
samples of water, as determined by the colour-meter
described in a previous report.

In Table III. we have recorded the oxygen required to
oxidise the organic matter in all the samples submitted
to analysis.

Of the 182 samples examined, the whole were found
to be perfectly clear, bright, and well filtered.

The proportion of organic matter present in the water,
though somewhat above that met with in the previous
months' supplies, continued low, especially for the season
of the year. The mean proportion of organic carbon
present in the Thames-derived supply was 0.167 part in
100,000 parts of the water, as against a mean of 0.140 part
in the supply of the previous month.

The several series of bacteriological experiments
described in our previous reports having been made with
water as supplied for domestic use, sterilised or not in
different instances, the series of experiments now to be
described was made with water taken directly from the
Thames and its tributary the Cherwell. In the conduct
of these experiments it was requisite both by preliminary
and contemporaneous study, to distinguish between
growths set up by the forms of microbe life proper to
running water, and those set up by the purposely intro-
duced *Bacillus anthracis*. In many cases the naked
eye differences were found not to be sufficiently distinctive,
but a recourse to microscopic examination, aided by a
staining of the growths with different dyes, always enabled
the nature of the growth to be satisfactorily determined.
Fourteen duplicate experiments, or twenty-eight infections
were made, but, one tube becoming accidentally broken,
only twenty-seven results were observed. The experiments
were made in the same manner as those previously de-
scribed. The proportion of infecting animal fluid formed, as
nearly as might be, 1-700th of the river water to which
it was added. The several infections were made in the
last days of June and early part of July, the temperature
of the water ranging from 68° to 71° F. (20° to 21.5° C.).

In the last recorded series of thirty-four infections, the
tubes of sterilised culture-fluid sown with the infected
water within half-an-hour of its having been infected, and
then submitted to incubation, exhibited in every case a
characteristic bacillar growth. But in the series now
under consideration, made with fresh river water, eighteen
out of the twenty-seven tubes of sterilised culture-fluid
sown with the infected water within half-an-hour of its
having been infected, exhibited on incubation, not any
growth whatever of the *Bacillus*; while even in the other

nine cases, the pathogenetic growth seemed more or less
attenuated by the various growths wherewith it was
accompanied. This result was quite in accordance with
the conclusion come to by other investigators, namely,
that in the struggle for existence, the microbe forms proper
to running water outgrow and starve out the introduced
morbific forms.

In each of the twenty-seven instances the sowings were
reported after an interval of six hours from the original
infection of the river-water, and in every case the sowing
proved to be infertile in respect to the foreign infective
bacillus; or in no case was the life of the bacillus in the
purposely infected river-water found to extend beyond six
hours, while probably in no case did it extend to anything
like so long.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 305.)

DR. JENKINS then brought up the subject of the Thomas-
Gilchrist Schlage, which he said were beginning to be
introduced into this country. As they contain phosphide
of iron, the phosphorus so combined would be oxidised
by nitric acid and determined as phosphoric acid. As the
amount reaches 1 per cent at times, this oxidation should
be guarded against.

DR. JENKINS also brought up the subject of the effect of
the presence of fluorine on the determination of P_2O_5 in
phosphates, such as fluorapatite. DR. WHITE said that
the small amount of fluorine in Charleston rock had been
found to make no difference.

Prof. MYERS then asked in regard to the presence of
silica in a soluble form.

Drs. JENKINS and WHITE and Prof. STUBBS mentioned
experiments in which the presence of silica to the extent
of 10 per cent had no effect. DR. WHITE then contributed
the following:—

*To Determine the Effect Silica in Solution has upon
Molybdate Determinations.*

A highly siliceous phosphate from South Georgia was
used. It contained total silica, 10.76 per cent.

	Per cent.
Dissolved by boiling in strong HCl	0.11
Dissolved by ignition with $Mg(NO_3)_2$ and solution in strong HCl	0.21

(a) 0.5 gm. was digested with 30 c.c. of concentrated
HCl, diluted, allowed to settle, poured off, the residue
repeatedly boiled with strong HCl, the fluids mixed, and
 P_2O_5 determined.

(b) 0.5 gm. was ignited with $Mg(NO_3)_2$, dissolved in
strong HCl, as above, and P_2O_5 determined.

(c) 0.5 gm. was treated as in (b), an aliquot of the
filtrate was evaporated to remove silica in usual manner,
and P_2O_5 determined. Results were as follows:—

	a.	b.	c.
Total P_2O_5	{ 22.54 22.58	22.65 22.60	22.59 22.61
Mean	22.56	22.63	22.60

The indications are that the small percentages of silica
brought into solution in the ordinary work of members of
this association do not appreciably affect the results in

* From the *Proceedings* of the Third Annual Convention of the
Association of Official Agricultural Chemists, at Washington, D.C.
August 26 and 27, 1886. Edited Clifford Richardson, Secretary.

P₂O₅. It may be assumed that it is not necessary to rid the solutions of silica.

DR. GASCOYNE found that the presence of silica had no effect on the determination of phosphoric acid by the molybdate method.

An experiment with a mixture of nine parts of acid phosphate and one part finely ground silica gave 14.93 per cent of P₂O₅ as the average of five determinations by the official method, and 14.92 per cent P₂O₅ as the average of five determinations of the nitric acid method. Three determinations, made by evaporating to dryness, igniting, and re-dissolving in HCl, gave 2.89 per cent as the average.

In discussion of these papers on the use of nitric acid instead of hydrochloric acid and magnesium nitrate, Dr. JENKINS said:—

The reasons which led to the adoption of hydrochloric acid as a solvent and magnesium nitrate as an oxidising agent are the following:—Hydrochloric acid dissolves all phosphates more rapidly, though not more completely than nitric acid, if sufficient pains are taken with the latter, but less time and watchfulness are needed when HCl is used, and for these reasons it has the preference. I admit that in many cases, particularly where alkaline salts are present, as in the ordinary grades of superphosphates, simple ignition will remove organic matter and leave all the phosphoric acid in the tribasic or orthoform. But in some cases it will not—as, for instance, in the case of South Carolina superphosphate in Dr. White's interesting table. Now our uniform method must cover all cases likely to occur, and therefore some basic oxidising mixture must be used unless organic matter can be destroyed in the wet way. Magnesium nitrate is the best mixture of the kind, for it does not flux silica. Dr. White's experiments, however, prove, I think, that the organic matter can be destroyed or sufficiently altered for our purpose in the wet way, and as that method is much simpler I favour its adoption.

Prof. STUBBS remarked that by accident it was found in his laboratory that HNO₃ could supplant Mg(NO₃)₂ in analyses of complete fertilisers. The fertilisers, consisting of cotton-seed meal, acid phosphate, and kainite, were ignited with HNO₃ and analysed. Being afraid of error, they were duplicated with Mg(NO₃)₂, and the results found to agree.

After some further remarks the committee was directed to prepare the outline of a method to be used during the ensuing year.

By unanimous consent it was then resolved that the President should appoint a committee to consider the advisability of extending the scope of the Association, to report later on.

The President appointed Dr. White, chairman, Dr. Jenkins, and Dr. McMurtrie.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 16th, 1886.

Dr. HUGO MULLER, F.R.S., President, in the Chair.

MESSRS. A. Percy Hoskins and M. Hunter were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Henry Coates, Hedon House, 11, Archway Road, Highgate, N.; Thomas Cooksey, B.Sc., 284, Pentonville Road, N.; Hamilton Emmons, Mount Vernon Lodge, Leamington, U.S.A.; Herbert McKeon, 123, Lansdowne Place, Brighton; J. F. McArthur, Belgrave Crescent, Eccles; David Henry Nayel, 21, Tay Street, Dundee; Joseph De Carle Smith, Jun., Norwich;

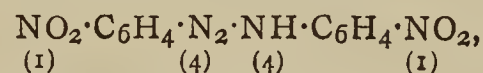
Lionel W. Stansell, 16, Hardy Street, Maidstone; D. A. Sutherland, Burntisland Oil Works, Burntisland, N.B.

The following were duly elected Fellows of the Society:—Messrs. Horace Edward Brothers; Francis J. H. Coutts; Tamemasa Haga; Henry John Hardy; Michitada Kawakita; Walter Leach; Stephen James Pentecost; Henry Joshua Phillips; P. Yeshwant Sheshadri; Tetsukichi Shimidzu; Joseph Stapleton; William Phillips Thompson; Hikorokuro Yoshida.

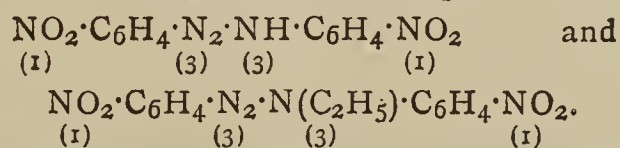
The following papers were read:—

116. "Researches on the Constitution of 'Azo- and Diazo-derivatives.' I. Diazoamido-compounds." By R. MELDOLA, F.R.S., and F. W. STREATFEILD.

In this paper the authors give the results of the application of the method described by them in a former communication (*Trans.*, 1886, 624) to determine the constitution of the diazoamido-compounds. The compound described in the previous paper, paradinitrodiazoamidobenzene, has the symmetrical formula

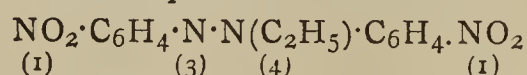


and is consequently unsuited for the settlement of the question of intramolecular migration of the N₂-group. An unsymmetrical compound has therefore been prepared from paranitraniline and diazotised metanitriline: it forms yellow needles melting at 211°, and furnishes on decomposition with chlorhydric acid a mixture of meta- and paranitranilines, and of meta- and paranitrochlorobenzenes. Its ethyl-derivative, prepared by the authors' method, melts at 148°, and gives on decomposition with chlorhydric acid a mixture of ethylmeta- and ethylparanitraniline, and of the two corresponding nitrochlorobenzenes. A method of identifying a mixture of meta- and paradiamines depending on the colour reaction on oxidation ("indamine" formation) is described in the paper. In order to throw some light upon the reaction which takes place when these compounds are decomposed by being heated with chlorhydric acid, experiments have been made by heating diazonitrobenzene chlorides with chlorhydric acid in the presence of similar and dissimilar nitrilines, but the products were found to be identical in all cases with those of the corresponding diazoamido-compounds, so that it appears probable that these latter compounds are actually formed in the first instance. Metadinitrodiazoamidobenzene (Griess, *Liebig's Annalen*, 121, 272) has been prepared by the action of 1 mol. proportion of NaNO₂ upon two of metanitriline dissolved in chlorhydric acid; it forms straw-coloured needles melting at 194°, and decomposes when heated with strong chlorhydric acid into metanitrochlorobenzene and metanitriline. The ethyl-derivative forms opaque whitish-yellow needles melting at 119°; it is decomposed by chlorhydric acid into ethylmetanitriline and metanitrochlorobenzene. The formulæ of these compounds are

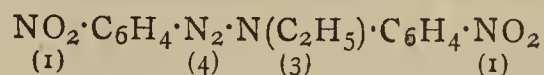


The next part of the paper deals with the question of the identity of mixed diazoamido-compounds. In accordance with the results obtained by Griess (*Ber.*, 1874, 1619) and other observers, it has been proved that the compound obtained by the action of diazotised paranitraniline upon metanitriline is identical with the above-mentioned compound formed by the action of diazotised metanitriline upon paranitraniline. The two compounds have the same melting-point (211°), and give the same products on decomposition by chlorhydric acid; the same holds good with respect to their ethyl-derivatives (m. p. 148°). From these facts it follows that in the formation of this compound isomeric change must take place in one or the other mode of preparation, and in order to throw light upon this question, the authors have prepared for comparison the ethyl-derivatives resulting from the action of

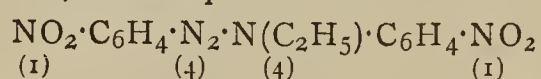
the diazotised nitranilines upon the ethylnitranilines. Thus by combining diazotised metanitraniline with ethylparanitraniline, a compound of the formula



is obtained. This is *isomeric* with the ethyl-derivative (m. p. 148°) above described; it melts at 174–175°, and is decomposed by chlorhydric acid into metanitrochlorobenzene and ethylparanitraniline. On the other hand, by the action of diazotised paranitraniline upon ethylmetanitraniline, the compound

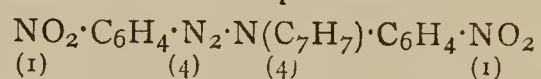


could not be obtained, but the product is apparently an amidoazo-compound forming orange-yellow needles melting at 187°. From diazotised paranitraniline and ethylparanitraniline, the compound

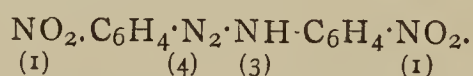


of m. p. 192°, described in a previous paper (*Trans.*, 1886, 630), is obtained. In a similar manner, diazotised metanitraniline acts upon ethylmetanitraniline with the formation of the diazoethylamido-compound of m. p. 119°, described in the present paper.

The further applicability of the authors' method has been tested by preparing benzyl-derivatives of the foregoing dinitrodiazoamido-compounds.



crystallises from benzene in small yellow needles melting at 190°; the corresponding modification 1 : 3 – 3 : 1 melts at 142, and the benzyl-derivative of the unsymmetrical dinitrodiazoamido-compound melts at 180°. The decomposition products of the benzyl-derivatives are analogous to those of the corresponding ethyl-derivatives. Summarising their results, the authors point out that the evidence obtained in the course of the present investigation shows a distinct tendency of the N₂-group to migrate to the para-position with respect to the other substituents: thus when metanitraniline is diazotised and combined with paranitraniline, the resulting compound has been proved to have the constitution



and not, as might have been expected on first consideration, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. This migration is possibly effected through the formation of an intermediate additive compound as suggested by Victor Meyer (*Ber.*, 1881, 2447), but the authors propose to submit this point to further investigation.

DISCUSSION.

Mr. FRISWELL asked did Professor Meldola invariably use the sealed tube method: might not a less violent method be employed? He thought that probably what had been said of the easy decomposability of some of the amido-azo-compounds referred to might be extended to all such bodies.

Professor MELDOLA in reply, said that it was not always necessary to heat in a tube: mere boiling sufficed in many cases.

117. "The Influence of Silicon on the Properties of Iron and Steel." Part I. By THOMAS TURNER, Assoc. R.S.M.

After referring to the work of previous observers in this direction, including Bessemer, Gautier, Mrázek, Pourcel, Riley, Snelus, and others, the author gives an account of experiments undertaken to determine the influence of silicon on the purest form of iron obtainable in considerable quantities. For these experiments metal was taken from the basic Bessemer vessel, at the end of the blow, and before any addition of manganese had been made. This metal had the following composition: C = 0.03, Si = 0.0098, S = 0.039, Mn = 0.06, P = 0.04. It was mixed in a red-hot clay crucible with varying small quantities of silicon pig, containing 10.3 per cent of silicon, the product being afterwards examined. The most important results are given in the table below.

Other specimens were prepared to which more silicon was added, but these broke in pieces in attempting to roll them. The last specimen in the above list is not comparable with the others, as in this case the silicon existed in the *oxidised* condition, and the material more closely resembled the original metal in its behaviour.

The author draws the following conclusions from his experiments. That the addition of silicon, in the form of silicon pig, to the purest iron obtainable in commerce tends to distinctly reduce its suitability for being rolled. With only a few hundredths per cent of silicon, the metal remains quiet in the mould. Red-shortness appears to increase with the amount of silicon, though the welding properties appear to be quite unaffected; the metal was tough when cold, with all proportions of silicon.

The limit of elasticity and tensile strength increase with addition of silicon, but the extension and the reduction of area are seriously diminished. The relative hardness is but slightly affected, and appears to be connected with the tenacity of the material.

With 0.4 of silicon and 0.21 of carbon a steel was obtained which was difficult to work hot, but could be hardened, and was very tough when cold. The author points out that these results would be considerably modified by the presence of larger quantities of carbon and manganese, such as are met with in practice.

DISCUSSION.

In reply to a question by Dr. P. Frankland, Mr. TURNER said that the high qualities of the sample which he had stated contained *oxidised* silicon (silica), were due not to the presence of this body, but to the absence of silicon.

The PRESIDENT asked if Mr. Turner could give any explanation of the boiling over, which he had referred to as occurring when the silicon-iron was added.

Mr. TURNER said that the matter had been somewhat fully discussed elsewhere, and it was generally believed to be due to the evolution of gas which the iron had been able to retain in consequence of its containing silicon.

118. "The Distribution of Nitrifying Organisms in the Soil." By R. WARINGTON, F.R.S.

The result of 69 experiments with clay or loamy soil from various depths shows that the nitrifying agent is present almost without exception down to 3 feet from the surface; samples from below this depth did not always exhibit the power of causing nitrification, and none of the samples of soil taken 8 feet from the surface produced

Si per cent by analysis.	Limit of elasticity. Tons per sq. in.	Breaking load. Tons per sq. in.	Ratio limit to break.	Extension per cent on 10 inches.	Reduction of area per cent.	Relative hardness.
0.0098	13.01	21.80	0.597	27.7	77.0	18
0.02	13.08	19.95	0.656	17.6	40.3	16
0.035	15.69	23.07	0.680	16.3	31.8	17
0.039	16.42	23.28	0.704	18.2	37.7	17
0.08	16.72	23.77	0.704	24.2	44.9	20
0.117	18.00	28.05	0.642	15.6	26.8	21
0.13	18.37	25.68	0.715	18.8	41.9	20
0.027	17.75	21.75	0.861	26.0	67.4	15

nitrification. The nitrifying organism present in the subsoil is apparently in a feeble condition, nitrification starting much later in solutions seeded with subsoil than in those seeded with surface soil. Reasons are given for believing that in agriculture nitrification is practically confined to the surface soil. The nitrogenous matter present in the subsoil is, however, nitrifiable if exposed to favourable conditions.

DISCUSSION.

Mr. PERCY FRANKLAND remarked that it appeared desirable to use a nutritive material more constant in composition than urine in experiments on nitrification. He objected to the term "nitrifying organisms:" Heræus, in Berlin, having recently proved that there were a considerable number of organisms capable of inducing nitrification.

Mr. WARINGTON said that, however unfit urine might be for a certain class of experiments, as the object he had in view was to ascertain if nitrifying organisms were present, he maintained that it was sufficient to have an easily nitrifiable solution. The President had asked—were nitrifying organisms present in essentially siliceous soils? He had no experience except with Rothamsted soils, but he should say that they were if such soils were found to contain nitrates; moreover, Müntz had shown that if the organisms once became established in a bed, whatever its nature, it became more or less capable of effecting nitrification in suitable liquids passed through it.

119. "Isomeric Change in the Phenol Series. The Action of Bromine on the Dibromonitrophenols." By A. R. LING.

The author's experiments have been conducted with the view of, if possible, obtaining some explanation of the isomeric change of dibromortho- into dibromoparanitrophenol by the action of bromine first observed by Armstrong (*Chem. Soc. J.*, 1875, 520). As products of the action of bromine on dibromonitrophenol he has obtained tetrabromoquinone, which is the chief product, together with bromo- and dibromoparanitrophenol and orthobromodinitrophenol; dibromoparanitrophenol and bromine yielding bromoparanitrophenol, orthobromodinitrophenol, and tetrabromoquinone.

It would seem that the formation of the bromanil involves the partial debromination of the dibromonitrophenol, the resulting bromonitrophenol then undergoing isomeric change: the bromoparanitrophenol thus produced is in part converted into bromodinitrophenol by the nitric acid resulting from the nitroxyl displaced in the formation of bromanil, and in part into dibromoparanitrophenol.

DISCUSSION.

Mr. GROVES asked if the author had tested his bromine for iodine; minute traces of this latter often had a most material influence: thus tribromophenol was readily converted into bromanil by means of bromine containing a little iodine, but not by pure bromine; and not a few other similar cases might be mentioned.

120. "Some Azines." By FRANCIS R. JAPP, F.R.S., and COSMOS INNES BURTON, B.Sc.

The authors have endeavoured to ascertain whether ditolane-azotide, $C_{28}H_{20}N_2$, and diphenanthrylene-azotide, $C_{28}H_{16}N_2$ (*Trans.*, 1886, 826 and 843), belong to the class of the ketines or to that of the azines. They find that no ditolane-azotide is formed when benzilmonohydroxim is treated with tin and hydrochloric acid, contrary to what might be expected to occur if the azotide were a ketine.

They further show that there is a close analogy between diphenanthrylene-azotide and Witt's α - β -naphthazine (*Ber.*, 19, 2794), and they have succeeded in synthesising the latter compound by heating β -naphthaquinone with ammonium acetate—a reaction which exactly corresponds with that in which diphenanthrylene-azotide is obtained from phenanthraquinone (*Trans.*, 1886, 829, foot-note). These analogies, together with the fact that ditolane

azotide may be transformed into diphenanthrylene-azotide (*Trans.*, 1886, 843), lead them to regard these compounds as azines.

CORRESPONDENCE.

AN EXAMINATION PUZZLE.

To the Editor of the Chemical News.

SIR,—It is obvious that A.X. derives his acquaintance of analysis chiefly from books and not from practical experience, or he would not expect to *precipitate* the ammonia by means of $PtCl_4$. He evidently does not understand the question, which means that potassium is absent. I should advise him to procure Clowes's "Practical Chemistry," and work according to the directions there given for the analysis of mixtures, and the next time he buys sodium silicate to ask for "soluble glass." I will not waste any more of your valuable space.—I am, &c.,

A.P.S.

["A. P. S." is mistaken in assuming that "A. X." is inexperienced. Were we at liberty to say who "A. X." is, he would be recognised as one of the most accurate and skilful chemists of the day, and the author of one of the leading books on Analysis.—Ed. C. N.]

CRYSTALS IN WHISKY.

To the Editor of the Chemical News.

SIR,—A closely felted mass of fine silky needles was brought to me some time since as having been discovered in a bottle of whisky. Analysis proved them to be Epsom salts, but in a form which was new to me.

I find that such a mass may be produced by mixing a solution of the salt with a proper proportion of alcohol, showing that the salt had been added to the whisky in aqueous solution.

A very pretty experiment on crystallisation may be made by adding methylated alcohol to a moderately strong solution of magnesium sulphate till a slight permanent turbidity appears, and immersing the vessel in cold water; stellate tufts of crystals soon separate, having about the same specific gravity as the liquid, in which they remain suspended, and rapidly grow till the whole liquid has become a mass of matted needles. If the turbid solution, before crystallisation commences, is poured into a watch-glass and examined under the microscope through an inch objective, the effect is remarkably beautiful.

I have determined the water in the fine light silky needles and find them to be $MgSO_4 \cdot 7H_2O$.—I am, &c.

PRACTICAL CHEMIST.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 23, December 6, 1886.

Action of Manganese on the Phosphorescent Power of Calcium Carbonate.—Edmond Becquerel.—Iceland spar is one of the first substances which presented to the author a luminous appearance in the phosphoscope after the previous action of luminous rays. The colour of the phosphorescent light is orange, but there are very

great differences in the intensity of the light emitted by different specimens. The presence of foreign matter can very much modify the phosphorescent power of certain bodies, and it was therefore important to examine if the differences of luminous effects given by various specimens of calc spar might not be due to the presence of a minute trace of foreign matter mixed or combined with the spathic calcium carbonate. The most luminous crystals of spar, orange in the phosphoroscope, contain a moderately high proportion of manganese, probably in the state of carbonate; there were scarcely any traces of iron carbonate. Fragments of calc-spar, still very luminous, contained manganese in less proportions, and less brilliant specimens contained only very little, or none at all if examined by ordinary analytical methods. Synthetic experiments lead to the same conclusion as the analysis of the natural crystals. These results show distinctly the action of manganese. Calcium carbonate obtained by dissolving fragments of Iceland spar in pure hydrochloric acid, even after several successive precipitations with ammonium carbonate, always led to the preparation of sulphides having an orange phosphorescence, whilst when the raw material used is arragonite the phosphorescence is always of a bright green. It is probable that the orange phosphorescence is either due to a double manganese-calcium carbonate, or to the fact that the presence of manganese gives to the calcareous compound a peculiar molecular arrangement, whence results a phosphorescent power more or less energetic, and a luminous emission of a given colour. This substance would then merely exalt the intensity of the light emitted by the spar. The author has shown that the crystalline form may interfere in these luminous reactions, since all the specimens of arragonite studied in the phosphoroscope emit a green instead of an orange light. Other bodies besides manganese can produce, in calcium sulphides, profound modifications in the intensity and the quality of the light emitted; such are lithium carbonate, bismuth, antimony, various sulphides, &c.

Composition of Cider.—G. Lechartier.—Pure ciders examined by the author contained 5 to 6 per cent of alcohol, 30 per cent of extract, and 2.8 per cent of ash.

Red Fluorescence of Alumina.—Lecoq de Boisbaudran.—Alumina, ignited and submitted to the effluve in a vacuum, did not give a trace of red fluorescence. This fluorescence was elicited by the presence of a trace of chromium sesquioxide.

Exploder Verifier of Quantity and Tension.—L. de Place and Bassée-Crosse.—This memoir cannot be intelligibly reproduced without the three accompanying diagrams.

Calorimetric Researches on Specific Heats and Changes of State at High Temperatures.—M. Pionchon.—The study of silver up to a temperature 200° above its melting-point gives a novel instance of the almost absolute identity of metals before and after fusion. In the three magnetic metals the variation of the specific heat reveals the existence of allotropic modifications. These changes of state take place in iron between 660° and 720°, and again about 1050°; for nickel, between 220° and 400°, and for cobalt about 900°. The law of Dulong and Petit cannot have the character of absolute strictness formerly ascribed to it.

Vapour Tensions of Solutions made in Ether.—Em. Raoult.—If we dissolve 1 mol. of any compound in 100 grms. of ether we diminish the vapour tension of this liquid by a constant fraction of its normal value; this fraction is 0.71 for all temperatures between 0° and 25°.

Volatilisation of Dissolved Bodies in the Evaporation of their Solvent.—P. Marguerite-Delacharlonny.—Liquid particles, holding salts in solution, are carried away with the vapour not merely at a boiling heat, but even at the ordinary temperature. The same process takes place from acid salts in the solid state, such as ferrous sulphate.

Researches on Bimetallic Phosphates and allied Salts, and on their Transformations.—A. Joly.—Many phosphates insoluble or sparingly soluble in water, may be obtained by double decomposition between a solution of disodic phosphate and a metallic solution. According to the nature of the metal the final product of the reaction is a trimetallic or a dimetallic phosphate. Thus, where the metallic solution is silver nitrate, we have at once a yellow amorphous precipitate of triargentic phosphate, and the liquid contains free acid. In the case of salts of calcium, strontium, barium, manganese, &c., the final product is a bimetallic crystalline phosphate. At the moment of mixing the two liquids we observe the formation of a gelatinous precipitate differing little in composition, if the solutions are sufficiently dilute from a trimetallic phosphate. The liquid is then acid to litmus, neutral to methyl orange, and contains a mono-metallic phosphate. The transformation of the initial gelatinous precipitate into a crystalline product results from an ulterior chemical action between the precipitate and the liquid.

Saturation of Normal Arsenic Acid by Magnesia and Formation of Ammonium-Magnesium Phosphate.—Ch. Blarez.—The author examines the mono-magnesium, bi- and tri-magnesium arseniates, in which the direct neutralisation-heats of a mol. of arsenic acid by magnesia, are, for the first equivalent, 14.866 calories, for the second 11.464, and for the third, 2.03.

Phenomena produced during the Heating and Cooling of Cast-Steel.—M. Osmond.—In melted iron containing 0.16 per cent of carbon, the author finds below 800° only a slight perturbation during cooling, about 749°. The cooling of cast-iron presents altogether three retardations; 1, between 863° and 820°, with a maximum between 845° and 839°; 2, between 775° and 736°, with its maximum between 763° and 749°; and 3, between 693° and 669°.

Influence of Silicon on the Condition of Carbon in Cast-Irons.—F. Guatier.—The author describes an alloy, ferrosilicon, containing at least 2 per cent of the latter element, which is grey, of a very compact grain, very fluid, and in every respect suitable for casting.

Water of Combination of Alums.—E. J. Maumené.—Ordinary potassium-aluminium alum contains 28.73 equiv. of water. If allowed to dry over sulphuric acid for 166 days it lost only 3.5 water, so that the assumed standard of 24 was not reached.

Neutralisation-Heat of Meconic and Mellitic Acids.—H. Gal and E. Werner.—The numbers furnished by meconic acid are lower than the corresponding figures for mellitic acid. This result might be foreseen, as meconic acid is an alcohol acid. The heat liberated in neutralisation diminishes as this process advances.

Moniteur Scientifique, Quesneville.

3rd Series, Vol. xvi., September, 1886.

The Industrial Preparation of Aluminium.—Dr. Mehner.—This paper is devoted to the process of Cowles Brothers, who reduce aluminium from its oxides by means of the electric arc. The demi-molecule of aluminium requires for its reduction 185,000 calories, which is more than carbon can furnish.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—London Institution, 5.

TUESDAY, 28th.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

THURSDAY, 30th.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

— London Institution, 6.
SATURDAY, Jan. 1st.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

THE CHEMICAL NEWS.

VOL. LIV. No. 1414.

THE ESSENITAL OILS: A STUDY IN OPTICAL CHEMISTRY.*

By J. H. GLADSTONE, Ph.D., F.R.S.

THE optical properties of the essential oils which are the subject of study on this occasion are their specific refractive and specific dispersive energy. These depend mainly upon their atomic constitution, while the power of rotating rays of light seems to depend rather upon the arrangement of the molecules.

The specific refractive energy is the refractive index minus unity, divided by the density. The specific dispersive energy is the difference between the refractive energy for two different parts of the spectrum, such as the solar lines A and H; or, more simply, the refractive index for H, minus that of A, divided by the density. The refractive energy multiplied by the atomic weight is termed the refraction equivalent. The dispersion equivalent is arrived at in the same way from the dispersive energy.

The data employed are given in the following Table, the first column of which gives the name of the substance, the second its molecular composition, the third and fourth columns the refraction and dispersion equivalents as determined by experiment. The refraction equivalent is calculated for the solar line A.

persion equivalent by about 0.5 in such substances as the olefines, or by about 0.8 in the aromatic group of bodies.

Bearing these figures in view, we arrive at the following conclusions from the optical data:—

1. That terpene hydrochlorate, terpene hydrate, camphor, and camphoric acid are saturated bodies. There are chemical grounds for the same conclusion in regard to each of these substances.
2. That terpene, notwithstanding the small amount of hydrogen, is nearly saturated, containing only one pair of doubly-linked carbon atoms. The theoretical equivalents will then be as given in the last columns, headed "Theoretical Value."
3. That isoprene, though it has only half the molecular formula, contains two pairs of doubly-linked carbon atoms, as shown similarly in the last columns.
4. That terpinol contains one pair of doubly-linked carbon atoms.

While these conclusions may be considered as fairly well established, there are others which must still be considered as speculative:—

- 1st. That there is a difference in chemical structure between terpene and camphene, indicated by the fact that, while both contain one pair of carbon atoms doubly-linked, the double linking in the camphene is analogous to that of the olefines rather than to that of the aromatic bodies. The theoretical figures on this supposition are given in the last columns.
- 2nd. That the citrenes differ from the terpenes by containing a second pair of doubly-linked carbon atoms, and that the double-linking of this second pair is also analogous to that of the olefines.

Substance.	Molecular constitution.	By experiment.		Normal calculation.		Theoretical value.	
		Ref. eq.	Disp. eq.	Ref. eq.	Disp. eq.	Ref. eq.	Disp. eq.
Terpenes	$C_{10}H_{16}$	73.0	4.0	70.8	3.2	73.0	4.0
Camphenet	"	71.9	3.7	70.8	3.2	73.0	3.7
Citrenes	"	75.0	4.6	70.8	3.2	75.2	4.5
Isoprenet	C_5H_8	40.3	3.2	35.4	1.6	39.6	3.2
Terpene hydrochlorate†	$C_{10}H_{18}Cl_2$	92.2	4.3	93.2	4.3	—	—
Terpene hydrate†	$C_{10}H_{22}O_3$	87.4	4.1	88.2	4.0	—	—
Camphor	$C_{10}H_{16}O$	73.5	3.4	74.2	3.4	—	—
Terpinol†	$C_{10}H_{18}O$	79.0	4.2	76.2	3.4	78.4	4.2
Eugenic acid	$C_{10}H_{12}O_2$	81.4	7.2	71.8	3.3	80.6	6.5
Camphoric acid	$C_{10}H_{16}O_4$	82.8	3.8	83.2	3.8	—	—

The law is now generally recognised that the refraction equivalent of a compound body is the sum of the refraction equivalents of its constituents, with certain limitations; and the same law seems to hold good in regard to dispersion equivalents. Now the refraction equivalent of carbon is 5.0, of hydrogen is 1.3, of chlorine 9.9, and of oxygen 2.8 or 3.4 (according to whether it is hydroxylic or aldehydic). Similarly the dispersion equivalent of carbon has been estimated by me at 0.25, of hydrogen at 0.045, of chlorine at 0.51, and of oxygen at 0.10 or 0.18.† Reckoning the value of the substances in the above Table by these numbers, we arrive at the figures given in columns 5 and 6 under the head of "Normal Calculation." It is at once apparent that while some of these are fairly coincident with the figures deduced from experiment, others are considerably divergent. This is explained by the fact that wherever there is a pair of doubly-linked carbon atoms the refraction equivalent is increased by about 2.2, and the dis-

- 3rd. That eugenic acid contains four pairs of doubly-linked carbon atoms, the theoretical figures being even then below those derived from observation.

ON THE COMPOSITION OF HYDRATED SALTS.

By E. MAUMENÉ.

To the Editor of the CHEMICAL NEWS.

SIR,

In the CHEMICAL NEWS of December 3rd I notice a paper by Messrs. Spencer U. Pickering and P. Sanford, in which these gentlemen profess to explain in a very simple manner (!) the results published some time back by me.

I have the honour of sending you an answer to the criticisms of my two honourable *confrères*. Pardon me for saying that the criticism is not worth of the subject.

I trust—not from any feelings of *amour propre*, but solely on account of the importance of the subject, which

* Communicated to the British Association, Birmingham Meeting, Section B.

† Prepared by Prof. Tilden.

‡ See my papers on "Essential Oils, No. III., their Specific Refractive and Dispersive Energy" (*Journ. Chem. Soc.*, 1886, p. 609); and "Sur les Equivalents de Refraction et de Dispersion" (*Arch. des Sciences Physiques et Naturelles*, September and October, 1886).

cannot be over-estimated—that you will be able to find space for my reply.

I remain, &c.,
E. MAUMENÉ.

91, Avenue de Villiers, Paris.

If this question appeared to chemists to be as important as it really is, we should spare no effort to solve it by experiments as accurate as possible, bearing in mind, at the same time, the precept “*Experientia fallax; judicium difficile.*”

Several chemists, and notably those in England, have recently examined this question with very great attention. Messrs. W. J. Nicol, W. A. Tilden, and others, have brought forward ideas, bearing more or less directly on the subject, quite recently. Messrs. S. U. Pickering and P. Sanford have advanced certain experimental studies as a help to a solution, which should be energetically upheld or opposed.

The best help is undoubtedly the General Theory which I respectfully brought before the notice of chemists almost twenty-three years ago, their indifference to which becomes daily more and more astonishing to me.

Messrs. S. U. Pickering and P. Sanford have just published (*CHEMICAL NEWS*, vol. liv., p. 277) several experiments professing to disprove the Theory.

The authors have actually found that one fact suffices to upset “in reason” a General Theory whose generality is so complete that it ought to require a large number of facts, but I hope to show very easily that the efforts of the critics have never been so far from attaining their ends; never, in trusting to one reason only, has the necessity for many and strong reasons been so blindly overlooked.

The Maumené Theory is of such universal application that it embraces chemistry in its entirety, without any exception,—lighting it with such a clear light that one must be most completely enveloped in the clouds of routine not to be enlightened by it.

All chemists, and especially English chemists, have recently had a startling proof of its applications, thanks to which I have been able to show that the General Theory enables us to explain *à priori*, and in all its details, the complicated (and previously unintelligible) chemical reactions of the pyrolysis of chlorate of potash.

It has been known, from the time of Terrellas, that this pyrolysis has a first phase which produces a salt whose acid contains more oxygen than chloric acid; it is perchlorate of potash which is produced.

In spite of numerous experiments, by which the truth was gradually coming to light, it was still admitted, and all the text-books taught as an *explanation* (!) the simple formula—



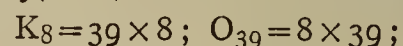
Instead of this classic formula, Teed—without knowing the General Theory, but having recognised by laborious experiments how far the above-mentioned was from the truth—took the trouble to establish the true formula by means of very accurately graduated pyrolyses. I will not here reproduce it, since it has already been given in the *CHEMICAL NEWS* only a year ago, with all necessary details.

I then made another appeal to chemists, and again brought under their notice the equation required by the General Theory, and published by me thirteen years before in *Les Mondes*. Its identity with the indisputable experimental equation found by Teed was most complete evidence, and ought by itself to have opened everybody's eyes. Messrs. Pickering and Sanford knew of this work, for they quote, among the examples of the General Theory which they try to combat, peroxide of potassium K_8O_{39} (or $\text{KO}_{4.875}$); peroxide of sodium Na_8O_{23} (or $\text{NaO}_{2.875}$), which I mentioned in the memoir relating to the chlorate.

They were also cognisant of my memoir on the alkaline hydrates, for they quote—

Hydrate of potash, $(\text{KO})_9(\text{HO})_{47}$,
Hydrate of soda, $(\text{NaO})_9(\text{HO})_{23}$.

They had therefore full knowledge of the two series of bodies, of which I was able to calculate the *true* formulæ *à priori*. I say *true*, because these formulæ have been established by different chemists and by myself by means of experiments of the greatest possible exactitude. The formulæ have an air of greatness due to their *simplicity*: $\text{KO}_{4.875}$, which does not appear “naturally to find an easy welcome among chemists” (why? my two *confrères* ought certainly to have said), is of extreme simplicity. This formula represents what we can imagine to be of the greatest simplicity, viz., a combination of equal weights,—



weights which are absolutely equal. It is just the same with regard to—

Na_8O_{23} ,
 $(\text{KO})_9(\text{HO})_{47}$,
 $(\text{NaO})_9(\text{HO})_{31}$,
 $(\text{BaO})_9(\text{HO})_{76.5}$,

and all analogous or possible compounds in all chemical reactions without exception.

If we refer to Gay-Lussac and to Thenard, we find KO_3 and NaO_3 for the peroxides; and if to Vernon Harcourt, we find KO_4 and NaO_2 ; but according to some experiments of my own, not yet published, I affirm that $\text{KO}_{4.875}$ and $\text{NaO}_{2.875}$ are the true formulæ of these peroxides.

As to the hydrates, $(\text{KO})_9(\text{HO})_{47}$ was given by Ph. Walter in the year 1836, twenty-eight years before the first publication of the General Theory. This formula was confirmed by my experiments in 1884, by the aid of two new methods:—

1. Desiccation of the hydrate by means of a hydrate of the same oxide, less rich in water: melted potash, &c.
2. Desiccation of the crystals at about 105°C ., in a very dry current of air, until the weight remains unchanged, for several hours, or even days.

The General Theory has been proved by many other facts no less indisputable, and to doubt it—which of course is quite permissible—cannot lead to its rejection without having very serious proofs, as thoroughly reliable as the experimental facts whose existence I have just recalled.

All compound bodies are in the general case in which the following holds good:—

From a chloride, CaCl , we get $(\text{CaCl})_9(\text{HO})_{55.5}$,
or $\text{CaCl}(\text{HO})_{6.17}$.

From a sulphate, SO_3MgO , we get $(\text{SO}_3\text{MgO})_9(\text{HO})_{60}$,
or $\text{SO}_3\text{MgO}(\text{HO})_{6.67}$.

From an alum, $\left\{ \begin{smallmatrix} (\text{SO}_3)_3\text{Al}_2\text{O}_3 \\ \text{SO}_3 \text{ KO} \end{smallmatrix} \right\}$ we get—
 $\left\{ \begin{smallmatrix} (\text{SO}_3)_3\text{Al}_2\text{O}_3 \\ \text{SO}_3 \text{ KO} \end{smallmatrix} \right\}_9(\text{HO})_{256.5}$,
or alum, $(\text{HO})_{28.73}$.

We admit in the case of—

CaCl , 6.000 HO, and not 6.17.
 SO_3MgO , 7.000 HO, „ 6.67.
Alum, 24.000 HO, „ 28.73.

But who can sustain “in reason” the truth of these figures, *apparently so simple*, but in reality so complex, as to be unknown; and what chemist is able to tell us *one word* about the combination of—

CaCl with 6 HO (really 6.17),
 SO_3MgO „ 7 HO (really 6.67),
or alum „ 24 HO (really 28.73)?

With regard to this latter figure, which has been most accurately found by my recent experiments on pure octahedric and pure cubic alum, dried by my method,—that is to say, by calcined alum, under the same shade,—I

have just added the last proof that crystallised alum kept under a shade with sulphuric acid loses its water very rapidly and very regularly, without for one moment remaining in the state corresponding to $24\text{H}_2\text{O}$.

I am forced to repeat myself:—The following examples, which are in no way specially selected, are taken from the most diverse classes of bodies,—peroxides, sulphates, hydrates, hydrated protoxides, hydrated chlorides, double sulphates, hydrated alums, &c. They are found in the whole range of chemistry without exception, because *the law of equal weights* is a *true law*, founded on simple calculation and free from all hypothesis.

To discredit "in reason" so beautiful a law, I ask all chemists, and above all Messrs. Pickering and Sanford, Have their experiments the slightest value? That crystals of NaCl retain a few thousandths of water at 100° I am perfectly willing to admit, but at 200° I deny it absolutely (according to some experiments made by me with extreme care in the year 1841). And further, I ask, Is it by adopting such illogical conditions (using fragments of a notable size, where these gentlemen explain themselves that the water was retained between the faces of the crystals),—is it by working in such a manner as to purposely cause mistakes, that anyone can decide the very grave question of the law of *equal weights*?

What it is necessary to prove and explain is that KO forms with HO , $(\text{KO})_9(\text{HO})_{47}$, &c.

These truths are proved by the General Theory, because all that results from a general law is proved. Does this proof want further experimental verification? Far from it; it agrees entirely with experience, for the more carefully the experiments are made the more closely they agree with the theoretic previsions.

Can Messrs. Pickering and Sanford deny one single result which has been predicted, explained, and proved by the General Theory? I say emphatically *No*, and I shall never be contradicted by experiments which serve to solve the great problem which is the basis of all chemistry.

STUDIES ON THE BEHAVIOUR OF THE PTOMAINES IN CHEMICO-LEGAL INVESTIGATIONS.

By K. TAMBA.

MORPHINE, in admixture with the ptomaines obtained by the author, can be recognised by the sugar and sulphuric reaction, the violet colour coming out distinctly; also with strong sulphuric acid on evaporation in the water-bath, and subsequent addition of hydrochloric acid, when a violet colour appears. In presence of ptomaines, iodic acid is reduced by morphine only when the ptomaines are present in mere traces. The other reactions of morphine are useless in presence of ptomaines.

The characteristic reaction of strychnine with potassium dichromate and sulphuric acid is not interfered with by ptomaines.

The nitric acid and the mercurous nitrate reactions are not affected by ptomaines, but that with nitric acid and sulphuric acid is interfered with.

With atropine the presence of ptomaines does not affect the reaction with nitric acid and alcoholic potassa, but it interferes with the odour characteristic of the action of sulphuric acid upon atropine.

The blood-red colouration of narceine with strong sulphuric acid does not appear in presence of ptomaines.

Fuming nitric acid colours the ptomaines a reddish yellow, but does not mask the characteristic violet colour of colchicine, if present.

Codeine in presence of ptomaines gives its reactions with sulphuric acid and with a mixture of sulphuric and nitric acids, but Frøehde's reagent is in this case untrustworthy.

Phosphoric and strong sulphuric acids in presence of ptomaines are useless reagents for aconitine (*i.e.*, the commercial qualities).

The sulphuric acid and ammonium bromide reaction for digitaline fails in presence of ptomaines.

The reactions for picrotoxine are interfered with by ptomaines, and delphinine cannot be recognised in their presence.

From further experiments the author concludes that the Stas-Otto method of extraction must always remain the first step. To be recommended is heating or distilling the acid extracts (after removal of the alcohol) with magnesia or lime hydrate to separate amines and volatile ptomaines. Basic lead acetate and recently precipitated lead hydroxide are well adapted for removing colouring-matters and other impurities from liquids occurring in judicial investigations, as they do not keep back any alkaloids. The use of powdered gypsum for drying up solutions for extraction with ether or chloroform does good service, as also the application of these general solvents for twelve or twenty-four hours at a boiling heat.

The ptomaines formed in the putrefaction of the liver and of masses of flesh can be almost completely separated from the alkaloids by prolonged extraction of the acidulated material with boiling ether, the ptomaines passing into solution. Ethereal solutions of alkaloids mixed with ptomaines can be separated by the addition of a saturated solution of oxalic acid in ether. On standing, the alkaloid is deposited as a crystalline oxalate, whilst the ptomaines remain in solution.—*Zeitschr. f. Anal. Chem.*, vol. xxv., p. 609.

NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF SULPHUR.

By M. VON KLOBULOW.

THE object of the process is the volumetric determination of the total quantity of sulphur in all such of its compounds as are capable of being decomposed by acids. The products of such decompositions are hydrogen sulphide, sulphurous acid, free sulphur, and, in certain special cases, sulphuric acid. The author finds that, under certain conditions, nascent hydrogen converts not only sulphuric acid, but even the sulphur liberated from some compounds quantitatively into hydrogen sulphide. Hence the principle of the method consists in the reduction of the decomposition-products of sulphur compounds by acids (always excepting sulphuric acid, which, if present, is determined in the ordinary manner) to hydrogen sulphide and its subsequent iodometric determination.

The conditions of the reaction are as follows:—

Sulphurous acid in solutions of a moderate degree of concentration is completely converted into hydrogen sulphide by nascent hydrogen at ordinary temperatures, or, better still, at a gentle heat, if air be excluded, and without any formation of sulphuric acid. The sulphur liberated on the decomposition of some sulphur compounds by dilute mineral acids is completely reduced to hydrogen sulphide in solutions of a moderate concentration, air being excluded, either at ordinary temperatures or preferably with slight refrigeration. In the author's method the sulphur compound in question is decomposed in a closed vessel in presence of zinc and hydrochloric acid. The sulphuric acid, which in some cases appears as a final product of the decomposition, remains in the apparatus, and is determined as barium sulphate along with any sulphuric acid pre-existing in the original sample; whilst the hydrogen sulphide, which always appears as the other final product, passes into suitable absorption-apparatus, filled with a titrated solution of iodine, the excess of which is titrated back after the operation. The apparatus used is as follows:—A capacious flask, holding about 500 c.c., in which the decom-

position of the substance is effected, is connected, on the one hand, with the absorption-apparatus, and on the other (by means of a tube reaching to the bottom) with a hydrogen-apparatus; a ball-funnel, fitted with a glass cock, permits of the introduction of the hydrochloric acid required for decomposition.

The absorption-apparatus consists of the following parts, arranged in the order mentioned:—A large flask in which the gas-delivery pipe from the decomposition flask reaches to the bottom, and which contains the bulk of the standard solution of iodine; a Liebig's potash-apparatus, also filled with standard iodine solution; a second potash-apparatus, filled with a solution of potassium iodide, in which any iodine vapour carried along from the former apparatus is absorbed. In carrying out the process a quantity of granulated zinc, free from sulphur and arsenic, is introduced into the decomposition flask along with the weighed substance in question or its solution, and diluted with a sufficiency of water. The flask is then closed, connected with the other pieces of apparatus, and hydrogen is passed in for about ten minutes to expel air, when the decomposition may be commenced. The zinc must be in excess, though too large a quantity makes the operation more tedious. The following cases must be distinguished:—

1. If there appears as decomposition product, besides hydrogen sulphide, free sulphur,—either alone or along with sulphurous acid,—the decomposition flask is placed either in a dish of cold water or in a vessel with a continual flow of water, and the decomposition is conducted as slowly as possible. Supposing the solution to be originally clear, it becomes milky in consequence of the liberation of sulphur, but this turbidity gradually disappears, and the liquid grows clear again. When the process has reached this stage, which occurs in twenty to twenty-five minutes, the cooling arrangement is removed, more acid is added, and the solution of the residual zinc is promoted by a gentle heat. When the zinc is completely dissolved the flask is heated for a time to 70° to 80°. The current of hydrogen (which does not need to be very strong as long as zinc is still present) is reinforced, and the liquid in the decomposition flask is thus kept in brisk motion, which, on the one hand, hastens the removal of the last traces of hydrogen sulphide from the liquid, and prevents a reflux of the absorptive liquid into the decomposition flask as the latter cools.

2. If, in the decomposition of the substance in question, there appears no sulphur, but merely sulphurous acid and hydrogen sulphide, any refrigeration is superfluous; the decomposition is begun at the ordinary temperature, and afterwards quickened by a gentle heat. In other respects the process is conducted as in Case 1.

Before breaking off the experiment it is well to ascertain, by means of lead-paper, if the sulphuretted hydrogen has been entirely removed from the flask. This test is best applied at the joint between the gas delivery-tube and the first absorption-apparatus.

The duration of the entire process is 1½ to 2 hours; after its completion the absorbent vessels are emptied into one common vessel, and the excess of the iodine solution is titrated back with sodium thiosulphate. The liquid in the decomposition flask contains all the sulphuric acid which has been formed during the decomposition, as well as that—if any—pre-existing in the substance. Its determination is effected in the ordinary manner. The solutions used are decinormal iodine and sodium thiosulphate standardised to each other. The hydrochloric acid used is of the strength 1 : 1.—*Zeitsch. f. Anal. Chem.*, vol. xxv., p. 555.

Agricultural Value of Reverted Phosphate.—Jules Joffre.—The author's experiments prove that precipitated phosphate, insoluble mineral phosphate, and reverted phosphate are all strikingly inferior in their efficacy to soluble phosphate.—*Moniteur Scientifique*.

NICKEL AS A MATERIAL FOR DISHES AND CRUCIBLES.

By J. ALFRED WANKLYN.

It is well known that pure nickel is one of the toughest of all the metals and that it fuses only at very high temperatures. It has a very fine grain, takes a high polish, and is very compact and unalterable.

These qualities have led to its being employed for crucibles and evaporating dishes. I have recently had some of these vessels in my laboratory.

The following notes may possibly be of interest to the readers of the *CHEMICAL NEWS*.

A small crucible of pure nickel, purchased at Becker's, in Maiden Lane, for 2s. 8d., weighed 17.6025 grammes. It was then ignited strongly by means of a large Bunsen burner, and when cold was re-weighed. Not the slightest alteration in weight could be detected.

A larger crucible, weighing 39.666 grammes, was also experimented upon, and exhibited a like constancy of weight on ignition.

For many purposes crucibles of pure nickel are quite as serviceable as platinum crucibles, and they are much cheaper, costing only about one-tenth as much as platinum.

They stand the action of alkalies remarkably well—there was no alteration in the weight of the crucible after caustic potash had been fused in it.

Hydrochloric acid in the cold, whether dilute or concentrated, may be used to clean out these crucibles and no alteration in weight is the result.

Cold oil of vitriol is likewise without action; but concentrated nitric acid attacks them, causing rapid loss of weight.

My experience leads me especially to recommend nickel dishes as suitable vessels for taking water-residues and milk-solids, and indeed for these purposes I do not think that nickel is at all inferior to platinum.

REPORT OF THE COMMITTEE *

APPOINTED FOR THE PURPOSE OF INVESTIGATING ISOMERIC NAPHTHALENE DERIVATIVES.†

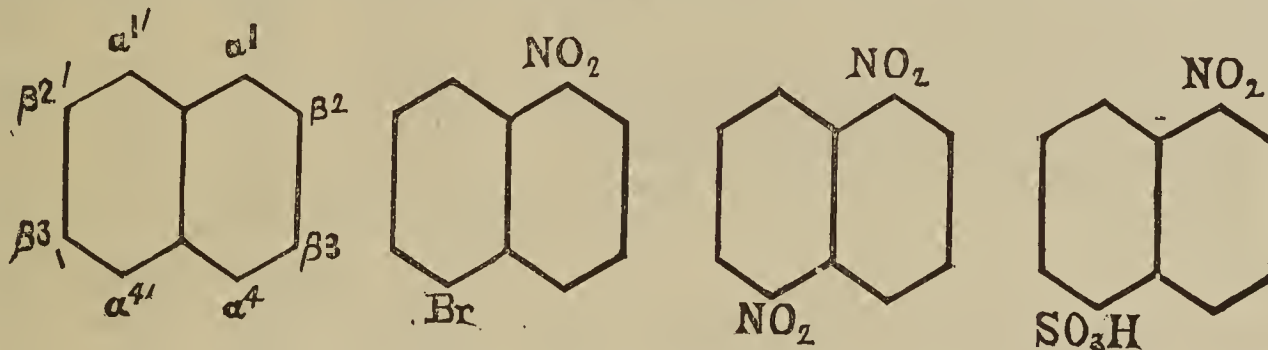
THE study of isomeric naphthalene derivatives acquires importance from a variety of considerations, notably from the very close relationship of naphthalene to benzene, which finds expression in the use of a simple hexagon to represent the latter hydrocarbon, the first mentioned being symbolised by a double hexagon formed of two benzene hexagons joined so that one side is common to both.

In the case of benzene there are but three possible isomeric di-derivatives, according to the received theory of the constitution of this hydrocarbon; the formation of these di-derivatives is governed by certain very simple "laws," the first of which may conveniently be termed the *para-law*, the second the *meta-law*: *i.e.*, mono-derivatives containing a hydrocarbon radicle, one of the halogens, NH₂, or OH invariably yield as *chief* product a *para*-di-derivative together with the isomeric *ortho*-di-derivative, the *meta*-di-derivative being formed, if at all, to but a small extent; whereas mono-derivatives containing NO₂, SO₃H, or COOH yield as *chief* product the *meta*-di-derivative, the *para*- and *ortho*-derivatives being formed in relatively small amount.

Instead of three, naphthalene may give rise to ten isomeric di-derivatives; it might therefore be expected that the laws of substitution for naphthalene would be proportionally less simple than for benzene; thus far,

* Consisting of Professors Tilden and Armstrong (Secretary).
† British Association, Birmingham Meeting, 1886.

however, this has not been found to be the case, and many of the di-derivatives are to be prepared only by indirect methods. The para-law obtains equally in the case of naphthalene, being applicable to mono-derivatives analogous to those which in the benzene series obey the para-law; but an interesting modification of the meta-law, exemplified by the behaviour of nitronaphthalene to bromine, nitric acid, and sulphuric acid, is to be noted: nitrobenzene under such circumstances would yield chiefly the meta-derivative, but in the case of nitronaphthalene the attack becomes shifted to the other nucleus, an α - α -derivative being formed as represented by the formulæ:—



It would appear from our knowledge of the naphthalene derivatives generally that, as a rule, the α -hydrogen atoms (see figure) are those which become displaced, and that the β -atoms are affected only under somewhat exceptional conditions—as in the formation of β -sulphonic acids at high temperatures in presence of an excess of sulphuric acid—and when an amidogen or hydroxyl group is present. Hence the behaviour of nitronaphthalene above referred to—the absence of similarity in the behaviour in the corresponding nitro derivatives of naphthalene and benzene—is not improbably due to the existence, in the case of naphthalene, of a higher law, which it may be permitted to term the “alpha-law.”

As naphthalene- β -sulphonic acid is the only β -derivative obtainable directly from naphthalene, it appeared to be specially important to study the behaviour of the sulphonic derivatives in order to throw light on the formation of the β -monosulphonic acid; and it was to be expected that their investigation would furnish results of value in determining the laws of substitution in the naphthalene series: moreover the ease with which the sulphonic radicle may be removed by hydrolysis renders the sulphonic derivatives especially suitable subjects of study.

It will suffice to indicate briefly the character of the results hitherto obtained, reserving a full account for one of the chemical journals.

The action of sulphuric acid in excess on naphthalene at a temperature of 160° — 180° has been studied by Ebert and Merz, who isolated two distinct acids—an α - and a β -disulphonic acid; Armstrong and Graham (*Chem. Soc. Trans.*, 1881, p. 133; *Berichte*, 1882, p. 204) on re-examining the product obtained evidence of the presence of other disulphonic acids, but after numerous trials the attempt to separate these was for the time abandoned, and attention directed to the preparation of disulphonic acids by other methods less likely to give rise to secondary changes, such as readily occur on heating in presence of sulphuric acid. The result has been to establish the existence of two acids isomeric with the α - and β -acid of Ebert and Merz.

γ -Naphthalenedisulphonic Acid.—This appears to be the sole product of the action of chlorosulphonic acid, ClSO_3H , on naphthalene in accordance with the equation: $\text{C}_{10}\text{H}_8 + 2\text{SO}_3\text{HCl} = \text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2 + 2\text{HCl}$. On distilling its chloride (m. p. 184°) with phosphorus pentachloride, γ -dichloronaphthalene is produced: therefore it may be concluded that γ -naphthalenedisulphonic acid is an α - α -derivative of the same constitution as the nitronaphthalene derivatives formulated above.

Naphthalene- β -disulphonic Acid.—This acid is prepared by acting on naphthalene- β -monosulphonic acid

with chlorosulphonic acid, and is certainly the chief product, but it remains to ascertain whether an isomer is not produced simultaneously. It is at once converted by the action of bromine into a dibromo-*monosulphonic* acid; this behaviour renders it more than probable that the sulphonic radicle introduced by the agency of the SO_3HCl assumes an α - position.

The two acids prepared by Ebert and Merz by the action of sulphuric acid at a high temperature (160 — 180°) are in all probability β - β -derivatives; they are both isomeric with the acids obtained by sulphonating naphthalene- α - and β -monosulphonic acids by means of

SO_3HCl ; and this difference being established between the action of sulphuric acid and that of chlorosulphonic acid, it appeared desirable to ascertain the behaviour with SO_3HCl of the naphthalene derivatives which had previously been converted into sulphonic acids in the ordinary manner. The derivatives taken were α -nitro-, α -bromo-, α -chloro-, and β -chloro-naphthalene: these have all been found to yield the same products when sulphonated by means of SO_3HCl as on treatment with sulphuric acid. It is especially noteworthy, however, that from both α -bromo- and α -chloro-naphthalene an acid has been obtained in small quantity isomeric with the *para*-sulphonic acid previously known, which forms the chief product; this secondary product is probably also an α - α -derivative like the primary product, but of the same series as the nitro-sulphonic acid formulated above. Two isomeric sulphonic acids also are obtained from β -chloro-naphthalene. One, which is the chief product when SO_3HCl is used, has been shown by Arnell to correspond to θ -dichloronaphthalene, while the other corresponds to ϵ -dichloronaphthalene, and therefore to the β -disulphonic acid of Ebert and Merz, and to Schaefer's betanaphthol-sulphonic acid. Probably θ -dichloronaphthalene is the ortho- or 1:2 modification, and it may almost be regarded as established that ϵ -dichloronaphthalene is a β^2 - $\beta^{3'}$ derivative; so that, while α - and β -chloronaphthalene both behave in the manner to be expected from the analogy subsisting between benzene and naphthalene, evidence is afforded by the production of the α^1 - $\alpha^{1'}$ -derivative from the one and of the β^2 - $\beta^{3'}$ -derivative from the other of the existence in the naphthalene molecule, in addition to the “para-plane” of benzene, of two “planes of symmetry,” as it were, in which an influence is exercised.

The study of the action of bromine on aqueous solutions of the naphthalene-sulphonic acids has also furnished results of interest. It has long been known that when naphthalene- α -sulphonic acid is treated with bromine the sulphonic group is displaced, dibromonaphthalenes being formed, whereas the β -sulphonic acid is converted into a dibromonaphthalene-sulphonic acid, the SO_3H group retaining its place. It now appears that this behaviour of the two acids is fairly typical. Thus the two disulphonic acids of Ebert and Merz—which are doubtless both β - β -derivatives—yield isomeric dibromonaphthaquinone-*monosulphonates* on treatment with bromine in excess—only one of the sulphonic radicles, viz., that which is contained in the C_6 group which is oxidised, being displaced. The isomeric dibromomonosulphonic acids obtained by treating (a) naphthalene β -monosulphonic acid and (b) the β -disulphonic acid above described with bromine are finally converted by the action of bromine into the same tetrabromonaphthaquinone, the sulphonic

radicle being displaced, although in the β -position, in consequence of the oxidation to quinone of the C_6 group in which it is located. The γ -disulphonic acid—which is doubtless an α - α -derivative—readily parts with both its sulphonic radicles, yielding as final products dibromonaphthaquinone and what appears to be a hexabromonaphthalene. A further illustration of the stability of a β -sulphonic radicle is afforded by the behaviour of (Schaefer's) betanaphtholsulphonic acid with bromine, the end product being a bromohydroxyquinone *sulphonate*.

The results thus briefly recorded have been obtained with the assistance of Messrs. F. W. Streatfeild, S. Williamson, and W. P. Wynne, B.Sc.

It is anticipated that by the time of the next meeting of the Association the investigation of isomeric naphthalene derivatives will have been carried sufficiently far to render possible a fairly complete statement of the laws of substitution in the naphthalene series in the shape of a final report.

ANALYSES OF COMMERCIAL FERTILISERS.*

(Continued from p. 319.)

THE report of the Committee on Potash was next submitted by the Chairman, Dr. Gascoyne:—

Report of the Potash Committee.

As required by the constitution of the Association the Committee on Potash herewith presents a brief report on work done during the past year. Last January your Committee sent six samples containing potash to fifteen official and commercial chemists, accompanied by the following circular letter:—

“Richmond, Va., January 6, 1886.

“Dear Sir,—In behalf of the Committee on Potash appointed by the Association of Official Agricultural Chemists at the Washington Meeting last September, I send you by express six samples containing potash, numbered 1 to 6, respectively.

“Please determine in them potash by the method adopted by the Association at the Washington meeting and also any other method you may desire to try. When the work is done please report results to me with detailed accounts of methods employed other than that adopted by the Association.—Very truly yours,

“W. J. GASCOYNE,
“Chairman Potash Committee.”

In the preparation of these samples chemically pure potassium salts were used, the materials very carefully mixed, and the samples sent to the members in sealed bottles.

The following is a description of the samples:—

No. 1. Potassium sulphate C.P.

No. 2. Commercial kainite.

No. 3. Acid phosphate, with pure potassium sulphate, sodium chloride, and magnesium sulphate, containing 2.70 per cent of potash.

No. 4. Acid phosphate, with pure potassium sulphate, potassium chloride, and potassium nitrate, containing 4.09 per cent of potash.

No. 5. Acid phosphate, with potassium sulphate, sodium chloride, and cotton-seed meal, containing 3.19 per cent of potash.

No. 6. Acid phosphate, with potassium sulphate, potassium chloride, and sodium nitrate, containing 2.25 per cent of potash.

The results are given in two tables, the first of which gives the results by the Association method, and the other by the method suggested by Mr. T. S. Gladding at the last meeting of the Association.

* From the *Proceedings* of the Third Annual Convention of the Association of Official Agricultural Chemists, at Washington, D.C. August 26 and 27, 1886. Edited by Clifford Richardson, Secretary.

POTASH DETERMINATIONS.

Association Method.

Analyst.	K ₂ O No. 1.	K ₂ O No. 2.	K ₂ O No. 3.	K ₂ O No. 4.	K ₂ O No. 5.	K ₂ O No. 6.
A ..	53.99	12.86	2.75	3.95	3.26	2.19
B ..	54.09	13.11	2.56	3.80	2.61	1.20
C ..	54.02	13.05	2.68	3.92	3.20	2.21
D ..	53.76	13.33	2.71	3.79	3.18	2.17
E ..	53.88	13.42	2.71	3.75	3.07	2.19
F ..	53.98	13.04	2.57	3.91	3.20	2.20
G ..	54.00	13.32	2.76	3.87	3.50	2.34
H ..	54.08	13.65	2.58	3.89	3.22	2.13
I ..	53.12	13.43	3.10	4.05	3.59	2.62
J ..	53.88	—	—	—	—	—
K ..	53.33	15.46	2.57	3.76	2.71	2.05
L ..	53.96	12.06	2.42	3.40	1.95	1.86
Average	53.88	13.33	2.67	3.83	3.03	2.10

Lindo-Gladding Method.

C ¹ ..	53.96	12.95	2.74	3.86	3.13	2.19
L ¹ ..	53.49	12.67	2.41	3.63	2.89	1.94
M ..	54.00	13.05	2.54	3.79	3.13	2.26
Average	53.82	12.89	2.56	3.76	3.05	2.13

In the table below are given the average results by the Association method, with the highest and lowest determinations:—

	Average.	Highest.	Lowest.	Difference.
No. 1	53.88	54.09	53.12	0.97
No. 2	13.33	15.46	12.06	3.40
No. 3	2.67	3.10	2.42	0.68
No. 4	3.83	4.05	3.40	0.65
No. 5	3.03	3.59	1.05	1.54
No. 6	2.10	2.62	1.20	1.42

In results by the Lindo-Gladding method, in sample No. 1, the difference between the highest and lowest determination is 0.51 per cent.

In No. 2 the difference between the highest and lowest determination is 0.38 per cent.

In No. 3 the difference is 0.33 per cent.

In No. 4 the difference is 0.23 per cent.

In No. 5 the difference is 0.24 per cent.

In No. 6 the difference is 0.32 per cent.

The report of the committee having been accepted, it was moved that the place of N. W. Lord, who was not present, be filled by the President.

He named Professor M. A. SCOVELL, of Kentucky.

Discussion being in order, Professors MCMURTRIE and CHAZAL stated their objections to the use of a porcelain dish for driving off ammonia salts and organic matter.

Professor SCOVELL said—Mr. President, I wish to call attention in the official method of estimating potash to the use of a porcelain dish in which the potash solution is brought to dryness and the ammoniac salts volatilise. In my own case I find it almost impossible to volatilise all the ammonia salts in a porcelain dish below a red heat, especially if not re-dissolved and re-ignited; this portion of the method is apt to mislead, and I would suggest the use of a platinum dish instead of porcelain. Unless great care is taken the results will be too high by the use of a porcelain dish.

Professors WHITE and MOSES called attention to the difficulty of washing the barium precipitate and the necessity of using boiling water repeatedly.

Dr. JENKINS said—A source of error in potash determination is this. In presence of a considerable quantity of alkali chlorides it is impossible perfectly to separate magnesia by barium hydrate, and if insufficient platinum chloride is used, the results obtained may be too high. The error may be avoided by adding in every case a very considerable excess of platinum solution.

Another and more common source of error is imper-

fect washing of the precipitate produced by BaCl_2 and Ba(OH)_2 . It is well known that BaSO_4 is apt to carry down with it soluble salts, and the gelatinous precipitate of barium phosphate is also hard to wash. I always use from 350 to 500 cubic centimetres of wash water, washing several times by decantation with boiling water before bringing the precipitate on a filter.

Professor CHAZAL objected to the fact that the use of the Gooch crucible should be required, and desired that the method of filtration should be optional.

Professor MOSES considered washing the double salt through the filter with hot water and afterwards evaporation and weighing as being as convenient as the Gooch crucible.

Dr. GASCOYNE called the attention of the members to the atomic weight of platinum by W. Halberstadt, in *Zeit. für anal. Chem.*, Heft 2, 1886.

Halberstadt gives as the mean of about 100 determinations 194.5759 as the atomic weight of Pt, thereby confirming the atomic weight as given by Seubert.

He also spoke upon the Lindo method as modified by Gladding, and recommended its examination by chemists, being confirmed by Mr. Richardson, who thought the use of the half-saturated solution of NH_4Cl , according to Gladding's method, would be found advantageous in any case. Dr. White suggested that the Gladding method be reported as an alternative, and also brought up the question of precipitating with barium chloride, hydrate, and ammoniac carbonate in an original portion of two grms. of the fertiliser without intermediate filtration.

Dr. WILEY said that on page 32 of the *Proceedings* for 1885 this had been abandoned.

Dr. RICHARDSON asked for opinions in regard to use of oxalic acid.

Mr. JENKINS saw no necessity, and gets higher results in kainite without it.

Professor MYERS said that he had made some comparative analyses, possibly thirty or forty determinations with the use of oxalic acid and without, using simply carbonate of ammonium.

Without having the figures with him he would state that the results appear to be equally accurate, except in the case of kainite, in which there is trouble unless oxalic acid is used, and even this fails, without care, to remove the impurities.

Dr. GASCOYNE found it useful in removing something not precipitated by ammoniac carbonate.

Professor SCOVELL thought the evaporation after addition of platinum should be carried further than a syrup, to remove all HCl , as he considered the double salt somewhat soluble in this.

Dr. JENKINS said he found there was no appreciable effect from this cause, but that going to dryness would produce no injury. The concentration of the alcohol used for washing was not vital.

On a question from Mr. Richardson, no objection was raised to the use of the old factors for the conversion of K_2PtCl_6 to K_2O .

(To be continued.)

NOTES ON THE ANALYSIS OF CHROME PAINTS.

By WALTER LEE BROWN.

HAVING had considerable experience, and not a little trouble, in the analysis of the above paints, I have thought the following notes might be of some aid to the student undertaking such work.

At first glance, and from merely reading over the directions given in the text-books, these analyses seem very simple and easy; they may be the former, but certainly not the latter. Much care and attention to detail are necessary.

The dry chrome paints come on the market in several forms, as lemon-chrome or chrome-yellow, orange-chrome, basic chromate of lead, and chrome-green. They can also be procured ground.

I. *Analysis of Mixed Chromate and Sulphate of Lead* (lemon-chrome or chrome-yellow).—Pulverise the sample, pass through a 100-mesh sieve, and mix. To 1 gm. in a small beaker add HCl and heat. Any insoluble matter (usually barytes as a gross adulteration) is to be filtered out, washed, ignited, and weighed. Further, its weight is to be deducted from that of the total lead weighed as sulphate.

Lead.—1 gm. is treated in a covered casserole with 25 c.c. concentrated H_2SO_4 , and heated moderately until the residue is perfectly white; cool, dilute with 50 c.c. water, and again cool; add 50 to 75 c.c. of 94 per cent alcohol, stir, and allow to stand one hour. Filter, wash with alcohol as usual, dry, heat, precipitate, and incinerate ash (after treatment with HNO_3 and H_2SO_4) half hour, heat again fifteen minutes, cool, and weigh. The successive weighings should not vary more than 2-10ths m.grm.

The process ordinarily performed with HCl and alcohol does not, in our hands, give good results.

The PbCl_2 formed will stay neither entirely on the filter nor in the filtrate, and causes trouble all the way through. After repeated trials we had to give it up.

Chromium and Sulphuric Acid (SO_3).—Treat 1 gm. with about 25 c.c. concentrated HCl , boil, dilute to 100 c.c., and while hot add excess of NH_4HO , which precipitates the chromium and the greater part of the lead. Boil off the excess of ammonia, filter, and wash very carefully with hot water.

Precipitate.— PbS reject.

Filtrate.—Boil off every trace of H_2S and precipitate Cr with NH_4HO in the usual manner. Put the moist precipitate and filter-paper into a crucible and ignite carefully. Weigh as Cr_2O_3 .

Precipitate for Cr.—Dissolve in dilute HCl , neutralise excess of acid with NH_4HO , precipitate Pb with H_2S gas, and filter into a porcelain dish.

Filtrate for SO_3 .—Acidify with HCl , concentrate, add boiling BaCl_2 drop by drop, and determine SO_3 as usual, taking care to wash very thoroughly with hot water.

Occasionally the following determinations are made:—

Water—hygroscopic. Heat $\frac{1}{2}$ gm. at 220°F . in air-bath to constant weight.

Volatile Matter.—Heat 1 gm. in porcelain crucible to gentle redness; loss, less water, is volatile matter.

Water Extract.—(Acetates, sulphates, bichromates, or nitrates of soluble salts, indicating imperfect washing.) Treat 3 grms. with six successive portions of 25 c.c. each of cold distilled water, decanting and filtering each time, and evaporate the filtrate in a platinum dish to dryness on a water-bath.

Calculations.—There are quite a few of these, and the use of factors, as shown by the following example, will save some little time.

Example.—21.62 per cent BaSO_4 obtained; $21.62 \times 1.3 = 28.10 =$ per cent PbSO_4 . $21.62 \times 0.888 = 19.19 =$ per cent Pb in the 28.10 per cent PbSO_4 calculated from the 21.62 per cent BaSO_4 .

Cr_2O_3 obtained = 16.87 per cent; $16.87 \times 4.241 = 71.54 =$ per cent PbCrO_4 .

$16.87 \times 2.716 = 45.81 =$ per cent Pb in the 71.54 per cent PbCrO_4 calculated from the 16.87 per cent Cr_2O_3 .

Total Pb (weighed as PbSO_4).. .. 64.45 per cent.

Pb belonging to the PbSO_4 19.19 ..

Pb remaining for PbCrO_4 45.26 ..

Pb calculated from the Cr_2O_3 45.81 ..

Difference 0.55 ..

The 45.26 per cent Pb calculated to PbCrO_4 ($45.26 \times 1.561 = 70.65$), which is considerably different from the 71.54 obtained from the Cr_2O_3 end. Theoretically, the

two chromates should agree; practically they will often differ, according to the complexity of the pigment. In such cases, and when delicacy of determination is not needed, or time is not available, the fairest way is to average, as one cannot always tell where to place the error. Thus the average of 71.54 and 70.65 = 71.09, this plus 28.10 per cent PbSO_4 gives a total of 99.19.

2. *Analysis of Mixed Chromate, Sulphate, and Carbonate of Lead* (lemon-chrome and white-lead).—Analysis made same as for 1; excess of lead is to be calculated as white-lead, $2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$.

Example.—A sample contained 11.47 per cent PbSO_4 and 48.78 per cent PbCrO_4 (the latter calculated from the Cr_2O_3). Pb in the PbSO_4 , 7.83 per cent, Pb in the PbCrO_4 , 31.22; the sum of these, 39.05, deducted from the total lead, 69.95, leaves 30.90; $30.90 \times 1.248 = 38.56$ = per cent white-lead.

Resumé: PbSO_4	11.47 per cent.
PbCrO_4	48.78 „
$2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$	38.56 „
	98.81 „

Water, volatile matter, and water extract not determined.

3. *Analysis of Orange Chromate of Lead* (chrome-orange).—Process same as for 1. Very little PbSO_4 will usually be found. Closer results will generally be obtained from this paint than from the mixed chromes.

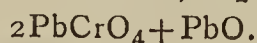
Example.—A sample recently examined gave PbCrO_4 from the Cr end, 99.41 per cent; from the Pb end, 99.34 per cent; difference, 0.07 per cent. Total analysis as follows:—

PbCrO_4	99.37 per cent (average).
PbSO_4	0.16 „
Volatile matter	0.50 „
	100.03

4. *Analysis of Mixed Orange Chromate, Sulphate, and Carbonate of Lead.*—Same as for 2. *Example:*—

PbSO_4	2.73 per cent.
PbCrO_4	71.40 „
$2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$	24.56 „
	98.69

5. *Analysis of Red Chromate of Lead* (known by many names, as scarlet, dark or basic chromate of lead, chrome red, Chinese red, red paste, American vermilion, and vermilion substitute).—Formula, $\text{Cr}_2\text{Pb}_3\text{O}_9$ or—



For the Pb determination take 1 grm. in covered casserole, add 25 c.c. concentrated HNO_3 , heat to boiling, and while boiling add half a dozen drops, one at a time, of alcohol, by means of a pipette; boil a while longer, add water, and all of the chromate, if it is pure, will be found to be in solution. Without this alcohol treatment great difficulty will be experienced in getting the chromate into solution; with it, it becomes very easy. Add 25 c.c. concentrated H_2SO_4 , evaporate to white fumes, and complete the analysis as described. For Cr and SO_3 determinations boil off alcohol and proceed as previously directed.

Calculations.—Calculate the SO_3 (if there should be any) to PbSO_4 , and the Cr_2O_3 to 2PbCrO_4 , and subtract their Pb from the total Pb, and figure the remaining Pb to PbO.

Example.— Cr_2O_3 obtained, 13.32 per cent = 56.49 per cent 2PbCrO_4 and 36.17 per cent Pb. Total Pb = 74.04 per cent; deduct 36.17 and 1.77 (from the SO_3 found), leaving 36.10 for PbO. $36.10 \times 1.077 = 38.87$ per cent PbO.

Resumé: $2\text{PbCrO}_4 + \text{PbO}$	95.36 per cent.
PbSO_4	2.60 „
Volatile matter and water	1.24 „
	99.20

6. *Analysis of Chrome Green.*—Composed of Prussian blue and yellow chromate of lead. The latter contains also sulphate of lead.

To 1 grm. of the sample add 25 c.c. HCl , heat to boiling several minutes, add water, allow to stand a while, then filter and wash thoroughly with hot water.

Residue.—Prussian blue (plus barytes or other insoluble matter, if present). Dry and ignite to Fe_2O_3 . Weight multiplied by 2.212 equals per cent Prussian blue. See Cr. det.

Filtrate.—Nearly neutralise with NH_4HO , leaving, however, the solution slightly acid. Pass H_2S gas through till Pb is all precipitated. Filter and wash.

Precipitate.—PbS. Dissolve on filter with hot dilute HNO_3 (1.4), and boil solution. Filter from collected S, and bring filtrate of $\text{Pb}(\text{NO}_3)_2$ to small bulk with several additions of H_2SO_4 . Evaporate to fumes of H_2SO_4 , cool, add water and alcohol, filter, wash and weigh as PbSO_4 as usual.

Filtrate.—For Cr (and Fe) boil off H_2S , add NH_4HO in slight excess, boil this off, and wash the $\text{Cr}_2(\text{OH})_6$ (and $\text{Fe}_2(\text{OH})_6$) as customary. Weigh precipitate as $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. After the weight is obtained mix with 1 part KNO_3 and 3 parts Na_2CO_3 , fuse in platinum crucible to clear fusion, cool, boil with water, filter, and wash.

Filtrate.—For Cr. Precipitate with NH_4HO in glazed porcelain dish as usual. If the weight of Cr_2O_3 is very nearly the same as before, then there has been no Fe extracted from the Prussian blue by the acid treatment. Some varieties are affected by this, others are not. If the weight is less than the original, deduct it from same; the result is Fe_2O_3 , which is also to be calculated to Prussian blue and added to the other.

Residue.—Filter, wash, dry, ignite, and weigh as Fe_2O_3 , if it is wanted as a check.

Sulphuric Acid.—One grm. heated with 25 c.c. HCl , filtered from Prussian blue, and SO_3 in the filtrate determined as directed under 1.

Calculations.—If there is more Pb than is sufficient to combine with all the Cr and SO_3 , and a qualitative test shows presence of CO_2 , then calculate excess of Pb to $2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$.

Example.—Prussian blue. Per cent of Fe_2O_3 obtained from the two separations as described, 1.755, multiplied by 2.212 = 3.88 per cent Prussian blue; per cent of Cr_2O_3 , 9.20 = 39.01 per cent PbCrO_4 ; per cent of SO_3 , 10.56 = 40 per cent PbSO_4 ; Pb in PbCrO_4 and PbSO_4 , 52.28 per cent: total Pb 65.54, deduct 52.28, remainder 13.26 per cent = 16.54 per cent $2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$.

Prussian blue	3.88 per cent.
PbCrO_4	39.01 „
PbSO_4	40.00 „
$2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$	16.54 „
Total	99.43

Table of Factors.

(Ba = 137, C = 12, Cr = 52.2, Fe = 56, H = 1, K = 39, N = 14, O = 16, Pb = 207, S = 32.)

Found.	Sought.	Multiply by factor.
<i>a</i>	<i>b</i>	$\frac{b}{a} = f$
BaSO_4 (233)	PbSO_4 (303)	1.300
BaSO_4 (233)	Pb (207)	0.888
Cr_2O_3 (152.4)	$2(\text{PbCrO}_4)$ (646.4)	4.241
Cr_2O_3 (152.4)	2Pb (414)	2.716
Fe_2O_3 (160)	$\text{K}_2\text{Fe}_2(\text{FeCN})_2$ (354)	2.212
Pb (207)	PbO (223)	1.077
Pb (207)	PbCrO_4 (323.2)	1.561
3Pb (621)	$2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$ (775)	1.248
PbCrO_4 (323.2)	Pb (207)	0.640
PbSO_4 (303)	Pb (207)	0.683
SO_3 (80)	PbSO_4 (303)	3.7875

With all these chrome paints a qualitative analysis should always precede, in order to make such modifications of the after treatment as may be necessary.

To determine the mixing fluid in any ground chromate, tare a small beaker and weigh into it from 10 to 15 grms. of the paint. Stir the paint three times with naphtha, using about 25 c.c. each time, and withdrawing the mixing fluid solution by means of a small suction pipette, such as is used for filling stylographic pens, &c. Finally, treat once with ether, withdraw same, dry beaker and contents, and weigh; loss equals mixing fluid.

References.—Fresenius's "Quantitative Analysis"; Rammelsberg's "Guide to a Course of Quantitative Chemical Analysis"; Wöhler's "Handbook of Mineral Analysis"; Normandy's "Commercial Handbook of Chemical Analysis"; "Simple Exercises in Technical Analysis" (entirely on Paints), in "English Mechanic and World of Science," London, from August 8th, 1884, to date, at intervals; "Painting and Painters' Materials," by C. L. Condit.

Credit is herewith given to my assistants, George H. Ellis and E. Speidel, and to E. M. Bruce, for the careful working out of the processes described in this article.—*School of Mines Quarterly*, October, 1886.

NOTICES OF BOOKS.

Select Methods in Chemical Analysis (chiefly Inorganic).

By WILLIAM CROOKES, F.R.S., V.P.C.S., Editor of the CHEMICAL NEWS. Second Edition, re-written and greatly enlarged. London: Longmans, Green, and Co.

A WORK written by the Editor of the CHEMICAL NEWS cannot, of course, be noticed in its pages in the same manner as one from any other source. Instead of discussing the merits or demerits of the work before us we must confine ourselves to point out its relations to the earlier edition, and to the whole scope of modern knowledge in analytical chemistry. In the first place the reader will soon perceive that the author has not attempted "to produce an encyclopædia of chemical analysis, in which is laid down every good method for the qualitative and quantitative examination of every known substance under every possible combination of circumstances." He has intentionally omitted: firstly, all methods and operations which are practised in every laboratory, and which are known to every student who has at all passed beyond the elementary stages; secondly, all procedures—possibly excellent—which he has not had the opportunity of personally verifying; and lastly, all such methods as are of questionable value. Such processes as many of our readers know possibly too well are neither few nor far between.

It will further appear that the analysis of organic compounds, qualitative or quantitative, industrial or purely scientific, has been left untouched. The vexed question of water analysis has also been omitted. Formulæ of any kind have been used only where required for the sake of identification, the author doubtless thinking, with Fresenius, that a treatise on chemical analysis is not the place for their ventilation. The various processes inserted have been, as far as possible, reproduced from the original memoirs, retaining the systems of weights and measures selected by their respective authors. The Centigrade thermometric scale has, however, been used, except where it is expressly stated to the contrary.

Among the essential features of the work, which have been not only retained but extended, must rank a number of little-known expedients and precautions—"shifts and dodges," as some chemists call them—which prevent mistakes, insure accuracy, and economise time. Such expedients are traditional in many of the leading laboratories, but they rarely find their way into abridged manuals and

text-books, and hence they do not always come to the knowledge of every student.

The new or improved features introduced in this edition include methods for gas analysis—a branch which has been greatly developed since the appearance of the first edition; the detection and isolation of the metals of the rare earths, a subject which has occupied much of the author's time during the last eight years, and with which he is still engaged; the separation of gallium from accompanying bodies; the novel indicators introduced in alkalimetry and acidimetry; the most recent improvements in the analysis of the metals of the platinum group and of phosphoric acid in commercial phosphates. There will be found further a great number of novel or improved methods for the recognition or determination of various bodies, which to catalogue would be alike tedious and uninteresting.

As far as can be traced out, little falling within the plan of this work, and appearing prior to date of its publication, has escaped notice.

The Glucosides. By Dr. O. JACOBSEN. Breslau: Trewendt.

THIS treatise is a reprint from the *Handwörterbuch der Chemie*, edited by Prof. A. Ladenburg, which again appears to be included in the *Encyclopædia of the Natural Sciences* (*Encyklopædie der Naturwissenschaften*) now being issued by the publisher above named.

The author defines the glucosides as compounds occurring almost exclusively in the vegetable kingdom, which, under various circumstances, take up water, and are split up into a sugar, and some other body not belonging to the sugars.

The sugars thus formed are either ordinary glucoses or special glucoses (some of which appear incapable of fermentation, and some optically inactive). Other glucosides do not yield a glucose at all, but bodies such as chinorite and isodulcite, which approximate more or less closely to the glucoses.

The glucosides are considered, generally speaking, as etheroid derivatives of the sugars in question. The bodies present along with such sugars or saccharoid bodies belong to very different groups, either of the aromatic or the fatty series. Thus we find hydrocarbons, alcohols, aldehyds, acids, diketones, nitriles, mustard oils, phenoles, and bases. In very many cases, however, the chemical nature of the bodies thus split off has yet to be determined. The decomposition is effected either by heating with a dilute acid—sulphuric, hydrochloric, or oxalic—with an alkali, or in some cases very slowly by boiling or superheating with pure water. The choice of the acid employed is not always a matter of indifference.

Ferments also, especially emulsine, have the power of splitting up glucosides, either at the ordinary temperature or with the aid of heat.

Some glucosides seem to contain in their molecule several sugar-residues which may be successively split off by treatment with dilute acids.

The signification of glucosides for the vegetable organism has not yet been determined. But it seems probable that glucosuccinic acid or, perhaps, several closely allied glucosides, must rank among the first products of assimilation.

After the introduction, of which we have thus given a brief sketch, the author proceeds to an enumeration of the glucosides in alphabetical order. He excludes, however, the tannins, which certainly yield sugars on boiling with dilute acids, but possess, in several respects, a distinct character.

Many of the glucosides, such as indican, quercetin, ruberythric acid, rutine, carminic acid, &c., possess a peculiar interest for the student of tinctorial chemistry, whilst others are of pharmaceutical importance.

As an appendix the author gives a very copious bibliography, giving references to no fewer than 649 memoirs.

May we add that we felt some pain on noticing how few of these references were to British authorities?

The Eleventh Annual Report of the Chemical Examiner's Department of the Government of Bengal. By C. J. H. WARDEN, M.D.

THE report deals with the work done in the year 1885, in which year 2343 analyses were performed, being about 400 less than the number done in the previous year; of these analyses 234 were of human viscera, the examination being for poison, 780 were for poisons in various substances, and 205 were for blood stains. Thus we find more than half the work done was in the detection of actual or suspected crime; more than 600 analyses were simply for finding the quality and purity of the articles, which were principally Government stores and ammunition. The results of all these analyses are very carefully tabulated and clearly expressed, and should be of great interest not only to chemists but to medical officers of health.

The appendix deals very thoroughly with the character and properties of the plant known as Madar (*Calotropis brocera*), which has very valuable medicinal effects. In syphilitic complaints it has been employed with such success as to be called "vegetable mercury." It is also exceedingly useful in reducing swellings, sprains, &c., and healing burns. The sap is very similar to gutta-percha, and has even some advantages over this latter substance, while the fibre itself makes an admirable substitute for hemp.

Whitaker's Almanack for 1887. By J. WHITAKER, F.S.A. London.

THIS useful book of reference is gradually assuming larger and larger proportions, each successive year seeing some addition and improvement. One of the distinguishing features of the latest edition of this almanack, which happily comes in Her Majesty's jubilee year, is the greater importance given to the colonial section. The scientific summary gives the latest news in the various branches of science. In speaking of M. Pasteur's experiments on the prevention of hydrophobia we note that out of the large number of patients treated less than one per cent. have died, assuredly a most satisfactory result.

In a paragraph on nitroglycerin and dynamite we read that the power exerted by an explosion on surrounding objects is in the inverse ratio of the cube of the distance from the point of explosion; that is to say, if the force of an explosion were represented by 1,000,000 on the spot, the force at 100 feet distance would only equal 1. The most recent discoveries of chemical elements are also given; 42 have been discovered from 1877 to the present time, of which 8 were found in 1886.

The whole almanack abounds with interesting and useful information.

CORRESPONDENCE.

AN EXAMINATION PUZZLE.

To the Editor of the Chemical News.

SIR,—The fact that A. X. is an experienced analyst renders his position all the more inexplicable. Surely, in an examination on the principles of analysis, the candidate is supposed to be acquainted with analytical methods! I never yet heard of an analyst who tested his ammoniacal filtrate with PtCl_4 without previous evaporation and ignition. There is nothing in the question referred to

which leads one to suppose that the PtCl_4 is added directly to the filtrate after separation of the precipitate produced by AmHo . On the contrary, does it not mention the group tests HCl , H_2S , AmHo , Am_2S_2 , Am_2CO_3 , followed by Na_2HPO_4 and PtCl_4 for Group V., plainly indicating that the usual course of qualitative analysis is to be followed?

Notwithstanding this, I maintain that if PtCl_4 were added directly to the ammoniacal filtrate it would give no precipitate, since the Am would be in a diluted condition.

As an experienced chemist, A. X. must know that there is more than one sodium silicate, and that the tetrasilicate ($\text{Na}_2\text{S}_4\text{O}_9$), when powdered, is readily soluble in boiling water.—I am, &c.,

A. P. S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. ciii., No. 24, December 13, 1886.

Glucose, Glucogene, Glucogeny, in Relation to the Production of Heat and of Mechanical Work in the Animal Economy. Sketch of an Absolute Determination of the Proportion in which the Combustion of Glucose contributes to these Phenomena. Part played by the Liver.—A. Chauveau.—The liver constantly supplies glucose to the blood. This glucose, incessantly yielded to the organs in the capillaries of the general circulation, constitutes the principal support of the organic combustions; the sources of animal heat and of muscular work for this support takes from the blood the greater part of the oxygen absorbed in the capillaries. Moreover, all the conditions which modify combustions modify, in the same direction, the quantity of glucose consumed by the organs. The production of heat and of mechanical work are so well connected in the animal economy with the glucogenic function and the combustion of glucose, that the liver pours this substance more abundantly into the blood when one or more sets of organs are in active work. Inversely, when at the extreme limit of prolonged abstinence, the liver no longer receives from the exhausted economy the materials necessary for the exercise of the glucogenic function, sugar disappears entirely from the mass of the blood, and we have cessation of combustion, a reduction of temperature, and death.

An Epidemic of Typhoid Fever at Pierrefonds in August and September, 1886.—P. Brouardel.—The well of the house which was most severely attacked is by far the least charged with organic matter (8 to 9 m.grms. per litre).

Thermic Phenomena accompanying the Precipitation of Bimetallic Phosphates and Allied Salts.—A. Joly.—The author here extends his researches to bicalcic phosphate, bibaric phosphates and arseniates, strontia diphosphate, and monobaric hypophosphate.

Neutralisation-Heat of Glyceric and Camphoric Acids.—H. Gal and E. Werner.—This short memoir does not admit of useful abstraction.

Certain Coloured Reactions of the Arsenic, Vanadic, Molybdic, and Arsenious Acids, also of Antimony and Bismuth Oxides.—L. Lévy.—After having indicated certain distinctive reactions for the titanitic, niobic, tantalic, and stannic acids, the author proceeds to describe the behaviour of other analogous acids under the same circumstances. Phosphoric acid gives no colouration. It is not the same with the arsenic, vanadic, and molybdic acids.

Reagents.	Arsenic Acid.	Vanadic Acid (before water).	Vanadic Acid (after water).
Morphine	—	—	Rose, then green.
Codeine.. ..	—	Slightly green.	Violet precipitate, soluble in excess of water.
Phenol	—	Sepia.	Sepia.
Thymol	Sepia.	Yellowish.	Rose.
Naphthol α	Green.	Green.	Light green.
Naphthol β	Brown.	Green.	Light green.
Resorcine	Sepia.	Black-green.	Violet.
Hydroquinone	Yellowish.	Yellow-green.	Green.
Pyrocatechine	{ Greenish grey, } then amethyst.	Black green.	Green.
Pyrogallol	Brown.	Sepia.	Rose.
Salicylic acid.. ..	—	—	Green.
Metaoxybenzoic acid	—	—	Rose.
Gallic acid	—	—	Greenish.

All the colourations due to arsenic acid are destroyed by water, save that produced by pyrocatechine; in this case we have a green liquid which is decolourised in course of time, giving a green precipitate. Molybdic acid colours only some of the above reagents: morphine becomes rose; resorcine sepia; codeine and the naphthols turn green; but all the reagents, if tested with the other acids, give, in presence of water, green precipitates. From the above table it is seen that we may clearly distinguish:—(1) Arsenic acid mixed with phosphoric and vanadic acid by the aid of pyrocatechine; (2) The latter substance mixed with its isomers by the aid of arsenic acid; (3) Vanadic acid mixed with molybdic and phosphoric acid by means of resorcine. Phosphorous, tungstic, and boric acids have no action, but bismuth and antimony oxides, as well as arsenious acid, yield coloured reactions.

Composition of the Sediment in the Settling-Tanks of Sugar Works.—Prof. Farsky.—The deposit contains 43.5 per cent of water, 0.0183 nitrogen, 0.9967 phosphoric acid, and 0.0356 potash.

Enrichment of Nitrogen in a Plot of Meadow Land.—P. P. Dehérain.—It appears that soils intensely cultivated become poorer in nitrogen, but grow richer again if the soil is planted with legumens and grass. This confirms the view that the want of plant-food in a soil cannot be determined by the constituents removed in the crops.

Determination of Ammonia in the Soil.—MM. Berthelot and Andrieu.—From the *Comptes Rendus*.

Action of Ferrous Oxide upon Vegetation.—Dr. O. Kellner.—The occurrence of readily soluble ferrous com-

Reagents.	Bismuth Oxide (before water).	Bismuth Oxide (after water).	Antimony Oxide and Arsenious Acid.
Morphine	Slight rose.	—	—
Codeine	"	—	Very pale lilac with arsenious acid alone.
Phenol	—	Rose.	Very slight rose.
Thymol	—	Rose.	Flesh.
Naphthol α	—	—	Green.
Naphthol β	—	—	Yellow.
Resorcine	—	Orange.	Sepia.
Hydroquinone	—	—	—
Pyrocatechine	Greenish.	Deep green.	Flesh.
Salicylic acid	Green, almost black.	—	Flesh.
Isomers of the preceding.. ..	—	—	—

The colours due to arsenious acid and antimony oxide disappear on the addition of water. The bismuth oxide must be quite free from nitro-compounds, which would furnish colours more intense. This table shows that by the aid of pyrogallol bismuth oxide may be recognised in presence of arsenious acid and antimony oxide. The same table, along with the foregoing, shows that arseniates may be distinguished from arsenites by pyrocatechine, whilst α -naphthol and water characterise tin in presence of arsenic, antimony, and bismuth.

Biedermann's Central Blatt für Agrikultur Chemie.
Vol. xv., Part 7.

Purification of Industrial Waste Waters.—Prof. Alex. Müller and Dr. Bodenbender.—The authors distinguish two methods of treatment: the cellular-chemical, which aims at removing organic impurities by setting up among them processes of fermentation and putrefaction; and the molecular-chemical, which is known in this country as precipitation. They point out that carbohydrates in sewage have an injurious effect upon vegetation and occasion acidity in the soil.

Determination of Organic Carbon in Soils which seize upon Free Nitrogen.—M. Berthelot.—From the *Comptes Rendus*.

pounds is to be regarded as a symptom of insufficient aëration of the soil, but such salts are not to be considered as directly injurious.

A Phosphatic Earth from Bergstadt.—Prof. Farsky.—This soil contains 36.024 per cent calcium phosphate, 7.240 ferric phosphate, and 0.968 aluminium phosphate.

Manurial Experiments with different Phosphates on Barley and Oats.—H. Sellschopp.—The exclusive use of Chili saltpetre gives the highest nett value of grain in the case of barley. Superphosphate and precipitated phosphate proved nearly equal both for barley and oats. Finely ground Gilchrist and Thomas slag proved inactive or even injurious.

The Efficacy of Chili Saltpetre as compared with that of Ammoniacal Salts according to the Experiments of Lawes and Gilbert.—Professor Maercker.—The author holds that the alleged injurious action of ammoniacal salts is for the present not demonstrated, and does not occur in normal conditions of the soil. Ammoniacal salts are best adapted for carefully cultivated clay-soils rich in clay.

The Formation of Fats in the Body of Carnivora from Carbohydrates.—Dr. Max Rubner.—The facts lead to the conclusion that fat may be formed from the carbohydrates in the bodies of carnivora.

Stone-Nut Waste as Cattle Food.—Dr. Loges.—These nuts are, in the author's opinion, poor in nutritive matter and of doubtful efficacy. Only 7 per cent of the carbohydrates can be regarded as easily digestible.

Moniteur Scientifique, Quesneville.
3rd Series. Vol. xvi., September, 1886.

German Review.—A memoir on para-amido-acetophenone, ortho-, amido-acetyl toluene, and certain derivatives of these bodies, by M. Klingel, taken from the *Berichte*.

Report on Alcoholism presented to the Academy of Medicine.—The consumption of distilled spirit increases yearly in France in an alarming manner, having doubled itself within forty years, and being to a great extent substituted for wine. The relatively mild drunkenness occasioned by wine has given place to the intoxication produced by distilled liquors containing a higher proportion of propylic, butylic, and amylic alcohols. "Fortified" wines are also rendered dangerous by the introduction of the higher alcohols.

The Naphtha of Baku.—Prof. Mendeleeff.—A consideration of these naphtha wells from a commercial point of view.

The Valuation of Manganese.—W. Atkinson.—From the *Journal of the Society of Chemical Industry*.

Volumetric Assay of Manganese.—J. Pattinson.—From the *Journal of the Chemical Society*.

On Maumené's Assay of Oils.—C. J. Ellis, F.C.S.—From the *Journ. Soc. Chem. Industry*.

Note on Maumené's Method for the Assay of Oils.—C. J. Ellis, F.C.S.—From the *Journ. Soc. Chem. Industry*.

On Saccharine.—With reference to the proposal to mix starch-sugar with saccharine, so as to bring up its sweetening power to the level of cane-sugar, Dr. Von Lippmann admits that the flavour of saccharine is often unpleasant, especially on prolonged use. Crude glucose (especially that made from potatoes) cannot be consumed as such on account of its bad taste. In Germany the sale of glucose mixed with saccharine, under the name of cane sugar, would be an infraction of the law.

The Progress of Chemistry and Mineralogy.—M. Friedel.—The Presidential Address delivered at the Meeting of the French Association for the Advancement of Science, held at Nancy, 1886.

Properties and Proprietors of Ungreenable Aniline-Black.—Camille Kœchlin.—A continuation of the Grawitz controversy.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xiv., No. 7, October 1, 1886.

Report on the Project of Supplying Paris with Water from the Springs of La Vigne and Verneuil.—A. Riche.—Paris is at present supplied with two kinds of water: an inferior quality, fit for industrial purposes, washing courts, coach-houses, watering gardens, &c., taken from the Seine above Paris, the Marne, and the Ourcq; and a better kind, fit for alimentary purposes, from the springs of La Dhuis and La Varne. The former kind is furnished at the rate of 172 litres per head of the population, and the latter only at that of 59 litres. In certain districts the two kinds are allowed to mingle. There are quarters where the spring-water is not laid on at all, and these include the barracks, the military hospitals, and a great number of schools. The water of the Seine, even above Paris, is contaminated by the drainage of starch works, distilleries, dépôts of night-soil, and manufactories of poudrette. The proposed supplies of water are drawn from the chalk. The analyses show

neither nitrates, nitrites, ammonia, nor organic nitrogen. The determination of bacteria has been made only at two of the springs. Their number is respectively 48 and 28.5 per c.c. Culture experiments have not been tried, the author considering this investigation unnecessary in the case of waters which have undergone a filtration so prolonged.

The Microbia of the Soil.—E. Laurent.—The author concludes that the action of the microbia is most useful in soils rich in organic detritus.

Preparation of Oxygen.—Into a gas apparatus are introduced 1 kilo. of oxygenated water at 3 per cent and 500 grms. of dilute sulphuric acid (1:5). Into this mixture is poured, by means of a funnel drawn out to a point and curved at its lower extremity, 56 grms. crystalline permanganate dissolved in 896 grms. of water. The yield is about 20 litres of oxygen.

Determination of Phenic Acid.—H. Beckurts.—The *Pharmacopœia Germanica* recommends a method due to Mr. Crookes, which consists in shaking up in a graduated tube a known volume of the phenic acid under examination with a dilute solution of caustic soda, and after settling to measure the volume of the hydrocarbon not dissolved. But as cresol and xylol behave in a manner very similar to phenol, Beckurts takes a measured volume of crude phenol, adds to it an equal volume of petroleum ether, and agitates in a graduated tube with a solution of 1-10th caustic soda. The petroleum ether renders the separation of the alkaline stratum more distinct, and it is easy to find by evaporation the quantities of neutral and resinous substances which it has dissolved. A part of the alkaline solution is introduced into a graduated cylinder supersaturated with hydrochloric acid, and the quantity of phenol set at liberty is determined. The separation of the phenol is complete only when the solution of sodium chloride is saturated, which renders it necessary to concentrate the alkaline solution of phenol down to the half its value. Phenol may retain 33 per cent of water and cresol only 15 per cent. Phenol retains about as much water as the solution of sodium chloride retains phenol.

Aluminium Oleate: its Use for Thickening Mineral Oils.—From the *Chemist and Druggist*.

Determination of Uric Acid.—Mr. Haycraft.—From the *Journal of the Chemical Society*.

Ulexine.—W. Gerrard.—From the *Pharmaceutical Journal*.

Phenyl-hydrazine.—M. Jaksch.—From the *Journal of the Chemical Society*.

The Vapour-Tensions of Bromine, Iodine, and Iodine Monochloride.—W. Ramsay and Sydney Young.—From the *Journal of the Chemical Society*.

MEETINGS FOR THE WEEK.

MONDAY, 3rd.—London Institution, 5.

— Medical, 8.30.

— Society of Chemical Industry, 8. "On the Explosive Kinetite," by Watson Smith; and other papers.

TUESDAY, 4th.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

— Pathological, 8.30. (Anniversary).

THURSDAY, 6th.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

— Royal, 4.30.

— Royal Society Club, 6.30.

— London Institution, 6.

FRIDAY, 7th.—Geologists' Association 8.

SATURDAY, 8th.—Royal Institution, 3. "The Chemistry of Light and Photography," by Professor Dewar, M.A., F.R.S.

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